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The principal objectives of the study are to examine potentially harmful consequences of element redistribution on the environment and to assess the opportunities for economic byproduct recovery of accessory elements. Attention is focused on mining and processing methods because of the important role of technology in the redistribution and recovery of accessory elements and compounds. The study also points out research needed for improving our understanding of envrionmental consequences and byproduct potential of large-scale mining activities. A principal reason for the study is the expectation that major increases in domestic production of many mineral commodities will occur, either as a result of changing national policies or actions abroad, which may result in important byproduct recovery. The report does not address health problems that might result from the redistribution of accessory elements, but it does discuss redistribution pathways through which toxic elements may reach the environment, thus providing an alert to potential health hazards. Five commodities, namely, coal, oil shale, uranium, phosphates, and alumina, were selected for study.

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PART II:
Uranium, Phosphate, and Alumina

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Redistribution of Accessory Elements in Mining and Mineral Processing

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PART II: Uranium, Phosphate, and Alumina

A Report Prepared by the
Committee on Accessory Elements

Board on Mineral and Energy Resources
Commission on Natural Resources
National Research Council

NATIONAL ACADEMY OF SCIENCES
Washington, D.C. 1979

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SUMMARY

INTRODUCTION

Scope of Study

The Committee on Accessory Elements was established to investigate the redistribution of accessory elements and compounds in future large-scale mining and processing of selected mineral materials. The principal objectives of the study are to examine potentially harmful consequences of element redistribution on the environment and to assess the opportunities for economic byproduct recovery of accessory elements. Attention is focused on mining and processing methods because of the important role of technology in the redistribution and recovery of accessory elements and compounds. The study also points out research needed for improving our understanding of environmental consequences and byproduct potential of large-scale mining activities. A principal reason for the study is the expectation that major increases in domestic production of many mineral commodities will occur, either as a result of changing national policies or actions abroad, which may result in significant impacts on the environment as well as on the potential for important byproduct recovery. The Committee does not address health problems that might result from the redistribution of accessory elements, but it does discuss redistribution pathways through which toxic elements may reach the environment, thus providing an alert to potential health hazards.

Organization and Procedure

A parent committee was organized to oversee the work of a number of panels, which were charged with investigating the redistribution problems associated with specific mineral commodities. Five commodities, namely, coal, oil shale, uranium, phosphates, and alumina, were selected for study. Individual panels, composed of four to eight members each, then investigated the problems associated with those commodities. The Coal Panel and Phosphates Panel held workshop meetings to assist in developing data for inclusion in panel reports, but the panels for oil shale, uranium, and alumina relied heavily on the literature and on private solicitations for their report input.

The Committee's overall report is divided into two parts. Part I, reflecting the special importance of fossil fuels today, combines the results of the Coal and Oil Shale Panels. Part II contains the results of investigations by the Uranium, Phosphates, and Alumina Panels.

The study is not intended to be a comprehensive assessment of all problems of redistribution or all byproduct recovery possibilities. Rather, selected commodities are studied to typify the range of possibilities and characterize the basic problems associated with increased production of mineral commodities. The selection of coal, oil shale, uranium, phosphates, and alumina for special attention is based on the expected growing importance of these commodities in the future economy of the country and the prospect of supply from domestic mining or the probable increase in the scale of domestic processing, with consequent potential for problems of redistribution of accessory elements and compounds.

In assessing the opportunities for byproduct recovery the Committee has looked primarily at the technological feasibility of recovery. It is recognized that, in addition to the market price for a product, any ultimate recovery also will depend on site-specific conditions and that to aggregate the potential byproduct production of an accessory element over total domestic production of a mineral commodity can be misleading.

Definition of "Accessory Elements and Compounds"

In this report the terms "accessory elements and compounds," "components," and "materials" refer to all constituents of a mineral deposit other than the commodity for which the deposit is primarily mined. In the usage adopted here, any one accessory element or compound may be present in amounts ranging from a trace to major proportions of a mineral deposit. Within the deposit the total of all accessory elements and compounds may be relatively small if the mineral material is of high grade. Conversely, the total may be very large if the deposit is low grade and requires the movement of huge volumes of material to recover primary materials sought. However, the problems of redistribution of accessory elements and compounds, particularly those with the greatest potential for adverse environmental impact, are only partly related to the volume of material produced. Of greater importance are the chemical nature of the materials redistributed and the transportation and dispersion mechanisms. Consequently, the chemistry of accessory elements, especially those occurring in relatively small amounts in an ore, has been given special emphasis in the various Panel reports. In addition to the naturally occurring accessory constituents associated with a mineral deposit, others may be introduced during mining and processing. These in turn may create new environmental problems from the redistribution of materials.

For this report the Committee has not adopted a single strict convention for the use of the terms "major," "minor," and "trace" to describe the quantities of accessory constituents present. However, in general it applies the term "major" to constituents present in quantities of 1.0 percent or more, "minor" to quantities in the range of

.01 to 1.0 percent, and "trace" to quantities less than .01 percent and commonly expressed in parts per million (ppm) or parts per billion (ppb).

GENERAL CONSIDERATIONS IN THE REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS

Geologic Factors Affecting Mining and the Redistribution of Accessory Elements and Compounds

Ore deposits form through geologic processes that redistribute elements and compounds into accumulations large and rich enough to be mined profitably. However, natural redistribution processes rarely segregate only the materials sought. Other elements and compounds, of little or no present value, are also accumulated. Thus, natural redistribution processes have to a greater or lesser extent predetermined the problems to be faced in taking mineral materials from the earth and preparing them for use. Some of the problems are related to the size, shape, and distribution of the ore body in space; some are related to the chemical nature of the minerals that comprise both the principal and accessory constituents; others are related to the physical properties of the ores and surrounding host rocks that must be removed, or exposed to air and water, during mining and processing. These natural physical and chemical features of ore deposits--the geologic characteristics--may strongly affect the subsequent redistribution of accessory elements and compounds in mining and processing operations. In general, small ore bodies of highly concentrated materials pose largely chemical problems in mining, beneficiation, and processing, whereas large ore bodies requiring the movement and treatment of huge volumes of material pose both chemical and physical problems.

Deposits formed at the land surface or subsea surface--so-called bedded ore deposits--are tabular or lenticular in shape, usually extend over wide areas, and ordinarily are covered by sediments. The thickness of these deposits may be measured in feet, but the areal extent may be tens of square miles. Of the commodities discussed in this report, coal, oil shale, phosphates and some non-bauxitic aluminum ores are of this type. Such deposits, originally flat-lying, may be tilted, folded, or even broken. Their present physical configuration, depth below today's land surface, and strength or weakness of rocks overlying them will determine whether mining can be best done by surface or underground methods. The sandstone-type uranium ores that contain the great bulk of uranium mined in the United States today resemble other bedded ore deposits from a geometric point of view, although they are more lenticular and individual deposits do not extend over such large areas.

Some ore deposits found in igneous bodies extend over large areas and contain relatively low concentrations of ore minerals that can be exploited only because they are amenable to very large-scale mining operations. Anorthosites and syenites, non-bauxitic sources of aluminum, similarly occur as igneous bodies of considerable extent that might at some future time become viable sources of aluminum by virtue of very large-scale mining operations.

Most ore-forming processes are chemical and characteristically concentrate the ore minerals as sulfides, sulfates, carbonates, or other compounds that can often be solubilized more readily than the silicates that comprise the bulk of the earth's crust. Hence, exposure of ore minerals to air and water during extraction and processing can lead to increased dispersion of the associated elements to the environment.

The physical setting of the ores and surrounding rocks influences the mining methods to be used in recovery of a particular mineral commodity. Near-surface deposits, such as the phosphates of the southeastern United States, are overlain by unconsolidated or loosely consolidated materials and can be mined readily from open pits. Deeply buried deposits, such as the coals of the Appalachians, require underground-mining methods. However, in the final analysis it is the combination of chemical and physical properties of the ores and surrounding rocks and the mode and scale of mining operations that establish the potential for detrimental effects on the environment or provide opportunities for byproduct recovery of trace or minor elements.

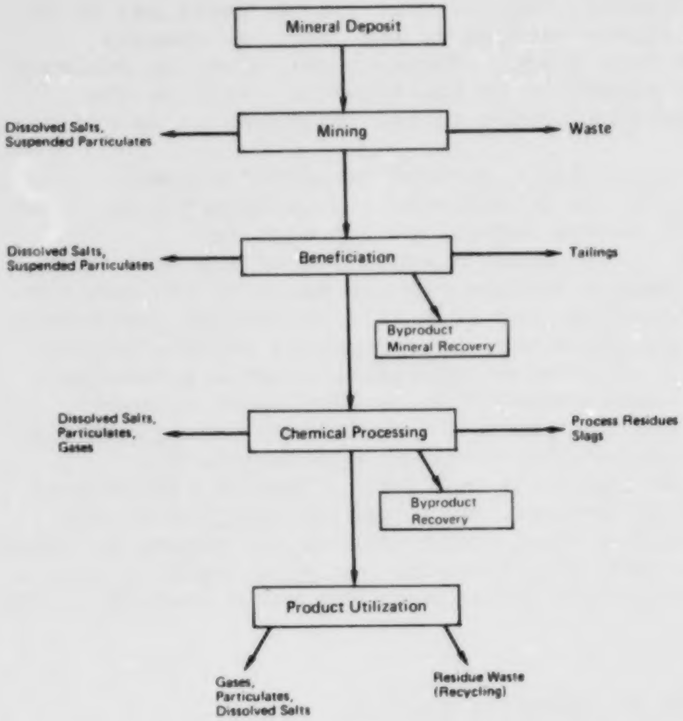
The Materials Cycle and Redistribution of Accessory Elements and Compounds

Once mining operations begin a mineral deposit is disturbed in such ways that many accessory elements and compounds are redistributed in markedly different patterns and concentrations from those that would occur by natural geologic processes. Redistribution of elements can occur during any of the steps involved in the materials cycle (Figure 1).

During mining, various elements and minerals, essentially unchanged, are made more accessible to environmental exposure. This initial increase in exposure is a result of comminution or size reduction during mining and gives rise to particulates that can be transported by air or water. Comminution also promotes the chemical reaction of minerals exposed to air and water, and commonly results in the production of oxidized water-soluble compounds that are transported as mine drainage. Waste rock or overburden is generally removed and piled away from the working area; some may be used in road and site construction but most goes into spoil piles. In surface-mining operations with high stripping ratios, significant amounts of overburden and mine waste are presently moved and even larger amounts are expected in future mining.

With most raw materials, the mined ore must be beneficiated to separate the desired minerals from the waste material. This is carried out first by comminution to a size at which the minerals are liberated from each other, followed by a concentrating mechanism for the desired ore minerals. Beneficiation technology utilizes physical or surface chemical means for separating minerals, and consequently the minerals are not changed chemically at this processing stage. Common methods of concentration involve flotation (wet process), gravity separation (usually wet), magnetic separation (wet or dry), electrostatic separation (dry), and flocculation (wet).

During beneficiation, size reduction is the most significant physical change in a raw material. However, separation of an ore into a concentrate (containing most of the desired product), and tailings (composed largely of unwanted materials), is the second stage in the


Mineral Deposit
Dissolved Salts, Suspended Particulates
Mining
Waste
Dissolved Salts, Suspended Particulates
Beneficiation
Tailings
Byproduct Mineral Recovery
Dissolved Salts, Particulates, Gases
Chemical Processing
Process Residues Slags
Byproduct Recovery
Product Utilization
Gases, Particulates, Dissolved Salts
Residue Waste (Recycling)

SOURCE: D. W. Fuerstenau, personal communication (1978).

FIGURE 1 Schematic flow diagram for materials through the materials cycle, beginning with their occurrence in the mineral deposit through their final utilization.

materials cycle where major redistributions of elements can occur. The concentrate may be utilized as the final product or, as in most cases, it is the feed material to subsequent chemical processing operations. One of the major complications of many beneficiation operations is that particles finer than 10 to 20 microns are not recovered. These fine particles can account for the loss, in some cases, of 10 to 20 percent of the valuable mineral in the ore. In addition to representing a wasted resource, their disposal may contribute greatly to air and stream contamination. Significantly, however, the beneficiation plant is the first stage in the materials cycle at which byproduct mineral recovery can occur.

Generally, chemical processing is required to convert the desired ore minerals into the chemical form suitable for use. In the case of a metal oxide, this entails reduction of the oxide to a metal, as, for example, in the production of pig iron in blast furnaces or the manufacture of ammonium phosphate in fertilizer production. Accessory element redistribution occurs through these chemical changes made in the materials. Elements in the metallic state, for instance, may accompany the metal whereas elements forming oxides may be separated and discarded as slag. In addition, volatile constituents can separate in a gaseous phase and be vented to the atmosphere.

In the processing of certain ores or concentrates, leaching with aqueous solutions may be a major separation step. Here, element redistribution follows from the discarding of leach liquid and any entrained leach residues. During chemical processing, there may be an opportunity to recover byproducts because of the chemical changes induced in the materials at this stage. Recovery can often be achieved by modification of specific processes in the flowplan, such as the installation of a dust collection system in the treatment of an effluent stream.

Product utilization accounts for a certain amount of element redistribution. Trace elements in fertilizers can be spread over large areas. Residual elements in metals and alloys can also be redistributed, depending on the eventual disposition of the materials.

Figure 1 schematically summarizes the flow of material through the stages of the materials cycle, that is, from (1) its natural occurrence in a mineral deposit, through (2) mining, (3) physical beneficiation, (4) chemical processing, and (5) product utilization (with potential recycle). Usually, all of these steps occur in developing a usable product, as exemplified by the production of fertilizer from phosphate ores. In the case of coal production for power generation, the beneficiation step is used to clean the raw coal. Chemical processing and product utilization would, however, be a combined step in boiler use. The production of coke from coal could involve all steps, as would commercial coal gasification and liquefaction. *In situ* gasification, however, would eliminate the beneficiation step and would combine mining with chemical processing.

PRECIS OF COMMODITY STUDIES

The following discussion summarizes the potential redistribution of accessory elements and compounds in coal, oil shale, uranium, phosphates, and alumina resulting from mining, processing, and utilization. Although there is currently no commercial exploitation of oil shale or non-bauxitic aluminum resources, these materials are discussed because of their potential use in the future production of oil and aluminum. Some of the information in the following summaries is recast later in the report under Central Findings and Observations to give special emphasis to certain topics such as potential environmental impacts and possible byproduct recovery.

Coal

In view of critical energy problems facing the nation today there is little doubt that coal will be used in increasing amounts in the years ahead. This increased use will not be without problems, particularly for the environment. There is a wide range of elements and compounds present in coals. These are redistributed in mining, beneficiation and burning, often in large quantities. The disposal of large volumes of wastes presents potentially serious environmental problems through the redistribution of proportionately large quantities of accessory elements and compounds. At the same time, however, there will be new and potential practices which, if diligently applied and studied, should significantly diminish these problems. Moreover, there will be enhanced opportunities for the byproduct recovery of various useful accessory elements and compounds.

In order to forecast the redistribution and recovery potential for different elements found in coal it is necessary to have representative data on total and average concentrations as well as the modes and variances of occurrence. Several factors influence the amount of an accessory element in a particular coal. These include: (1) composition and source of the original peat, clay, and other minerals added during and after organic matter accumulation; (2) chemical and biochemical changes through geologic time; and (3) hydrologic interchange with surrounding rocks. Despite the increasing availability of data on the distribution and concentration of trace elements in different coals the information is insufficient to permit a definitive assessment of trace-element occurrence or potential for redistribution. Yet, certain elements, such as arsenic, boron, barium, antimony, and selenium, can be identified consistently with certain coals, and patterns of occurrence are beginning to emerge. Some coals show local or regional enrichment in such elements as cadmium and zinc.

Most trace elements occur in coals in quantities less than their crustal abundances. It is in the associated shales and clays that the higher concentrations of many elements occur. This may require special attention to coal-cleaning processes to prevent or minimize the wide redistribution of deleterious constituents during burning. On the other hand, coal-cleaning wastes will become enriched in elements such as cadmium, chromium, copper, fluorine, mercury, nickel, lead, and zinc. There is little quantitative information upon which to base estimates of the composition of such wastes presently or on the disposition of these elements ultimately.

Slightly over half of the coals mined in the United States are not cleaned before use, so there is an escape of some mercury, selenium, fluorine, sulfur, boron, chromium, vanadium, and even radionuclides in present stack emissions. Large increases in the use of coal as a fuel for conventional boilers or new devices such as fluidized-bed combustion units also will increase the problems faced in disposing of elements in wastes such as ash, fly ash, slag, and products of stack-gas scrubbing. Many of the elements that escape in stack emissions or end up in waste may pose problems to the health of plants, animals, and humans. Many elements are found beneficial in some degree to certain types of plants under specific conditions. However, some are known to be detrimental to plant growth and others may be at higher levels of concentration. Prominent among troublesome stack emissions from coal-fired boilers is sulfur. Stack emissions can be transported long distances in the atmosphere and may be deposited as acid rain. The control of some stack emissions is difficult because many elements and organic compounds are concentrated on particles too small to be trapped by conventional stack-gas cleaning methods.

Coal-conversion processes, now under study in pilot and demonstration plants, raise questions of health effects that are not yet clearly understood. For example, tars produced from coal gasification and liquefaction contain relatively high concentrations of lead, arsenic, and titanium as well as organic compounds known to be carcinogens. Commercial-scale testing of control equipment is likely to be needed before we know how effectively accessory elements and compounds are removed from process streams in proposed coal-conversion operations.

The burning of increased tonnages of coal for the production of electricity will result in unprecedented quantities of solid wastes requiring environmentally acceptable methods of disposal. The solid wastes can be expected to be a major sink for many trace elements and accessory compounds, including mineral species not present in the raw coal but introduced from the country rock or developed through chemical reactions of combustion or pyrolysis. The solubility of trace elements and accessory compounds in solid wastes is believed to be as important in the redistribution into the environment as is their total concentration. We do not at present have sufficient understanding of the complex interactions responsible for the solubility, mobility, and attenuation of trace elements from coal wastes. Nor do we have much indication of whether or not various coal solid wastes and their leachates, under certain conditions, are hazardous to the biota.

Thus, leaching of contaminants from coal-waste piles is a concern, but as yet we are unable to fully interpret its nature. Recent laboratory studies show that leachates, produced under a variety of conditions, contain concentrations of boron, calcium, potassium, manganese, ammonium, lead, sulfate ions, and antimony, in amounts exceeding the water quality standards set by the U.S. Environmental Protection Agency (EPA). (In some cases, such leachates might be diluted only to a minimal extent in ground waters because of limited flow and mixing.) However, in these same laboratory experiments, a number of trace elements in leachates were immobilized by passage through earth materials. Fly ash also has been found sufficiently soluble to yield leachates under certain conditions that exceed acceptable water quality criteria for arsenic, boron, vanadium, cadmium, chromium, manganese, and selenium.

Various methods of disposing of coal wastes have been considered. Particular attention has been given to disposal in surface and underground mines. However, such disposal may increase acid mine drainage and/or increase the solubility and mobility of many accessory elements in the wastes. In addition, the effluents from coal wastes may contain appreciable amounts of processed organic matter, such as coal-liquefaction residues, and there may be some toxic products associated with them. On the other hand, increased accessibility of some trace elements may be beneficial to plants, animals, and humans under certain conditions, and care should be taken to identify the beneficial as well as the deleterious aspects of accessory elements redistribution.

There is considerable potential for byproduct recovery of accessory elements from coal products, and future mining and processing should consider this potential. Trace-element recovery from coal-preparation-plant refuse may be economically attractive because the cost of mining and most of the preparation costs may be charged to the coal and not against the byproduct. However, it is difficult to assess the prospects of economic recovery of accessory elements because the amounts and distributions of those elements at a site are incompletely known, and the market conditions determining value will vary widely. Except for sulfur, there is only limited information on the concentrations and distributions of accessory elements and compounds in coal wastes. With better data it will be possible to estimate the extent to which future problems created by increased amounts of wastes associated with coal mining, beneficiation, and burning can be offset through the recovery of mineral materials from coal-waste products.

Oil Shale

Oil shale resources in the United States are very large and probably contain more than 2 trillion barrels of oil, although much of this is probably not recoverable. No commercial-scale production of oil from oil shale is yet under way, but the future development of this resource could supply a significant part of the U.S. oil requirements over the long term. This in turn will require the mining and processing of vast quantities of raw oil shale and the disposal of resulting waste products. Because there has been no industrial development of oil shale, our knowledge of accessory elements and their redistribution is limited. Yet, some basic data on accessory element content is available and this, together with knowledge obtained from pilot and large-scale retort tests, permits an identification and assessment of many of the problems that will be faced in future exploitation of our oil shales.

The principal oil shale reserves of the United States are found in the Green River Formation of Utah, Wyoming, and Colorado. They contain relatively high concentrations of an insoluble organic material, kerogen, from which the oil is derived. Locally, halite, nahcolite, and dawsonite are present in the shale in potentially commercial quantities. Nahcolite is a potential source of soda ash and dawsonite a source of aluminum. A wide spectrum of trace elements is associated with oil shale deposits and the potential for element redistribution is high. Because of low rainfall and the high concentration of salts associated with mineral strata in the Utah-Wyoming-Colorado region, surface and ground waters contain large quantities of dissolved salts leached from the shales and associated strata. For many of these waters the content of sulfur, chlorine, fluorine, boron, iron, arsenic, and manganese exceeds public health standards before any industrial development is undertaken.

Oil shale may be mined by open-pit or underground methods and subsequently retorted above ground, or it may be retorted by _in situ_ methods. Each method disturbs large quantities of material and increases the probability for redistribution of accessory elements. Open-pit and underground mining may require the disposal of highly saline subsurface water as well as the disposal of huge volumes of waste rock. The main problems in the disposal of overburden from open-pit mining or waste rock from underground mining involve leaching of soluble minerals, which could contaminate surface and ground waters. Erosion of waste piles could also be a problem.

The extraction of oil from oil shale will be accomplished through underground _in situ_ retorting or by surface retorting. _In situ_ processes would retort 75 percent or more of the rubblized shale in underground retort chambers. If the chambers are sealed from groundwater zones, the redistribution of elements would be limited to pyrolysis products removed from the retort as gases and liquids.

The composition of gaseous products would depend on the composition of the oil shale, the retort temperature, and the composition of air used to support combustion. Low-Btu gas produced in the retort primarily contains nitrogen, carbon, oxygen, hydrogen and sulfur. There is little information on the trace-element content of the gas phase, but it is likely that mercury, arsenic, selenium, and possibly fluorine will be present. Water vapor condensed from the gas phase contains primarily ammonia and carbonates, with traces of some organic substances and sulfur-bearing compounds. If these gases were used to generate electrical power, the resulting nitrous oxides, sulfur dioxide, carbon dioxide, and water in the off-gas would probably be emitted to the atmosphere.

Liquid products are principally shale oil and retort water which is volatilized with the oil and must be physically separated. Accessory elements in shale oil from simulated in situ retort tests include arsenic, cadmium, fluorine, selenium, sulfur, nitrogen, iron, nickel, cobalt, mercury, phosphorus, and titanium. However, little data are available on how these elements might be redistributed. In situ process demonstrations have resulted in retort waters containing ammonia, carbonate and bicarbonate, sulfur, chloride, and dissolved or suspended organic compounds. Smaller quantities of calcium, magnesium, and sulfides are present, as are suspended shale fines. Trace elements in retort water include arsenic, boron, fluorine, mercury, and selenium.

If underground retort chambers are not sealed, a new set of potential problems will exist because liquids and retorted shale leachates may have access to ground waters. The use of a mixture of ammonium nitrate and fuel oil as an explosive for rubblization prior to retorting could also result in enrichment in nitrogen, which, as nitrate, is highly soluble and hence a possible ground-water contaminant.

Surface retorting will also result in the redistribution of elements into gaseous and liquid phases of the process stream, and in addition will generate large volumes of retorted shale that will require disposal in an environmentally acceptable manner. Presently available qualitative data suggest that most of the trace elements, including beryllium, cadmium, chromium, cobalt, fluorine, lead, manganese, molybdenum, nickel, vanadium, and zinc, are retained for the most part in the retorted shales. However, arsenic, nickel, vanadium, and zinc are also redistributed to the oil in significant quantities. Arsenic, mercury, selenium, and zinc have been detected in the off-gases. Particulate emissions during crushing and moving the raw shale may also result in some redistribution of elements. Fluorine is especially likely to be an important element in particulate emissions.

The main potential for byproduct recovery in the mining and processing of oil shales lies in the recovery of aluminum from dawsonite and soda ash from nahcolite. It is possible that the treatment of dawsonite by leaching processes would result in the redistribution of elements associated with the dawsonite. But nahcolite is unchanged chemically by crushing, sorting, and screening to recover the fine nahcolite particles. Some commercially valuable sulfur, ammonia, and petroleum coke might be obtained from the shale oil when it is treated to reduce its nitrogen and sulfur content prior to pipeline transportation.

Redistribution of accessory elements during oil shale processing will occur primarily in the disposal of waste products. Three major solid and liquid waste products--off-gas scrubbing wastes, retorted shale, and retort process water--will require disposal. There may also be some prerefining wastes generated.

Off-gas scrubbers will contain carbon, nitrogen, and sulfur along with some trace elements. The composition of the wastes will depend on shale composition and retorting variables such as the extent of gas recycling, which will vary in turn with location and retorting technology. The disposal problems with retorted shale are notable because of the huge volumes of waste, as much as a million or more tons per day, that might be produced by a mature industry. Redistribution of trace elements could occur through loss of particulates by wind and water erosion, and by leaching of retorted shales. Due to the physical properties of retorted shale, erosion losses will be substantial if waste piles are not stabilized. Disposal of retorted shale or in situ retorting close to the water table or within the saturated zone would present opportunities for the redistribution of elements and consequent ground-water pollution. Except for arsenic, fluorine, mercury, and perhaps antimony, most trace elements are retained in the retorted shale, but only limited information is available on their leachability with time or their possible environmental impact. Preliminary studies indicate elements most likely to be leached are fluorine, molybdenum, arsenic, and lithium.

Potential problems related to organic residues in retorted shales, such as complexing of trace elements and solubilization of organic residues, as in the case of inorganic residues, will depend on processing methods, management of wastes, and environmental variables. Several investigations are now under way to establish the effects of these variables on the mobility of inorganic and organic residues.

A foremost environmental concern in the leaching of retorted shale is the potential impact on the salinity of the Colorado River. Lower Basin salinity might be increased by reducing the flow of water into downstream regions. Uncontrolled mine dewatering, runoff from retorted shale disposal piles, or percolation of saline leachate into local hydrologic systems would also increase Lower Basin salinity. These effects might well be greater in drought years. On the other hand, the withdrawal and subsequent treatment of large volumes of highly saline water from saline aquifers or surface streams might decrease the salinity of the river.

Prerefining wastes could also result in the redistribution of accessory elements, but prerefining practices are not well established and data on the compositions of these wastes and on the potential movement of accessory elements are very limited.

Uranium

The mining and processing of uranium ores pose special problems with respect to environmental hazards because of the radioactive nature of certain accessory constituents. Unlike many other mineral commodities the future mining of uranium is not apt to involve a large total volume of ore. It is anticipated that as much as 85,000 short tons of ore per day may be milled by 1985 and perhaps twice this amount by the year 2000, depending on the acceptance of the nuclear power option in the years ahead. Part of the increased tonnages mined will result from an increased demand for uranium fuel, but part will result from the lower grade of ore that is expected to be mined. Nevertheless, the total tonnages will remain modest and compared to other commodities the redistribution of accessory elements as a result of mining and processing can be expected to be of limited volume. The uncertainty of the future demand for uranium fuel makes it difficult to make a rigorous assessment of the problems of element redistribution. However, it is possible to identify and evaluate the kinds of problems that will be involved in future mining of uranium ores.

It can be expected that domestic uranium production will continue to come from coarse clastic rocks, about half of which will be mined by surface methods and half by underground methods. Elements associated with uranium ores from sandstone-type deposits include selenium, vanadium, molybdenum, iron, cobalt, copper, beryllium, arsenic, nickel, lead, silver, and zinc, plus the daughter products of natural radioactive decay of uranium. The range of element concentrations is rather broad and reflects the erratic occurrence of specific elements in sandstone-type deposits. The amounts of these elements in uranium ores is known with some degree of certainty only for the Colorado Plateau ores. Only very limited information is available on ores from other mining districts.

Some elements associated with uranium ores are essential to our industrial economy, but all have sources of supply much greater than that involved in U_3O_8 production. Some vanadium, molybdenum and copper have been recovered as a byproduct of processing some sedimentary-type ores, but in general there is little incentive to recover accessory elements except when this is necessary as an environmental or product purity consideration. Some molybdenum has been recovered and marketed as calcium molybdate or ammonium phosphomolybdate. Copper has been recovered in some past uranium-milling operations, but presently only one plant has copper recovery facilities. Vanadium has likewise been recovered from some past milling operations. At current prices there is an incentive to recover this element only if it occurs in mill feed in amounts of .2 percent or more. In the Uravan mineral belt vanadium is present in quantities that make recovery worth considering.

Attempts have been made to extract some elements such as rhenium, scandium, and selenium in uranium ore processing, but the prospects for economic recovery are remote or nonexistent in today's markets. Thorium-232 has been recovered as a byproduct or coproduct of uranium processing in other countries, but no U.S. ores contain enough of this element to be worth recovering. It has, however, been present in sufficient quantities to require care to prevent contamination of the uranium product.

The major concern in the redistribution of accessory elements associated with uranium ores involves the loss of radioactive products to the environment. About 85 percent of the natural radioactivity is contained in the tailings that result from processing. Mining and milling make the radionuclides more available to water, plants, and animals via losses from finely ground tailings in waste dumps. Exposure may result from windblown dust containing thorium-232 and radium-226, inhalation of radon-222 (radon gas), gamma radiation, or contamination of ground waters.

Disposal of wastes is thus a significant problem to be resolved in the future mining of uranium ores. The nature of this problem will not change with the mining of increased tonnages of ore but the magnitude will. Care must be taken to stabilize or isolate radioactive waste products. It has been found that a clay cap over tailings can substantially reduce the exposure from radon-222.

Some earlier mining and milling operations resulted in excessive ground radiation near old tailings piles. There has been, in addition, some contamination of stream waters with radium-226, selenium, and vanadium--to the extent that water quality did not meet state water quality standards for irrigation or livestock. A covering of the waste piles can lessen greatly such contamination of the environment. It seems likely, however, that most of the past problems involving the redistribution of accessory elements in mining and processing uranium ores can be minimized in the future through strict adherence to current environmental regulations.

Two processing methods, variations of acid leaching and alkaline leaching, are used to recover uranium. The occurrence of byproduct-type elements in the ores is completely incidental to the operation and is of importance only insofar as they affect the processing costs. Rarely are accessory elements worth recovering for their income potential, but it may be necessary to give them special treatment to avoid product or environmental contamination.

It is likely that most future mining and processing of uranium ores will be carried out with technology now employed. An exception to this is the possible further development and application of *in situ* recovery methods in which uranium is leached underground from the host rocks. *In situ* leaching might mobilize accessory elements such as arsenic and selenium in the ore and ground waters might then become contaminated. Our knowledge of the effects of *in situ* processing, however, is very limited.

Phosphates

Phosphates provide a major underpinning of our agricultural industries and are thus one of our most vital resources. The United States has large reserves of phosphates and is not dependent on foreign imports. Most of these resources are located in the coastal plain of Florida, Georgia, and North Carolina, and in the western mountain states of Idaho, Montana, Wyoming, and Utah. Lesser resources are present in Tennessee. Most of the domestic deposits are mined by open-pit methods and most of the phosphate product goes into wet-phosphoric acid manufacture and ultimately into fertilizers.

Phosphate mining and processing operations result in major redistributions of accessory elements and compounds. A perspective of the magnitude of potential redistribution problems, both in terms of environmental impact and byproduct recovery of associated elements, may be gained from the fact that the United States produced about 47 million tons of phosphate rock in 1977. This quantity of phosphate rock contained 5 to 10 thousand tons of accessory uranium, an amount that is significant even though the average uranium content of phosphate rock is only .01 percent or slightly more. Redistribution problems begin with mining operations when uranium-bearing waste rock is excavated and moved to other locations where radon gas may escape into the atmosphere unless the waste material is buried or capped with a layer of nonradioactive overburden. In beneficiation of phosphate rock, where the matrix is crushed and treated to recover phosphate concentrates, large quantities of wastes, both as coarse tailings and as very fine materials called slimes, are produced. More importantly, accessory elements and compounds are redistributed to these wastes. Although most uranium is contained in the pebble and concentrate products, significant amounts are lost in slimes and lesser amounts in sand tailings. This redistribution of uranium and its decay products, like that in spoil piles, is of note because of radon emissions that could adversely impact on land use and habitation.

It is in the chemical processing of phosphate concentrates that most opportunities for redistribution of accessory elements and compounds occur. In acidulation processes, especially, many elements and compounds become highly mobile and find their way into stack gases, process waters, and process solid wastes, and to lesser extent into recovered byproducts and manufactured products. Of particular importance is fluorine which makes up 3 to 4 percent of the phosphate concentrates and which can impact adversely on the environment if allowed to escape. Large quantities of fluorine are evolved in wet-phosphoric acid production and find their way into stack gases. However, these gases are scrubbed to remove most of the fluorine, although small amounts of this element do escape into the atmosphere. Fluorine may also migrate via process waste water to gypsum settling ponds where most of it is precipitated and contained as solid-waste products. There may be some fluorine emission into the atmosphere from storage-pond waters, and escape through ground-water seepage is also a possibility. However, fluorine emissions are now carefully controlled by state and federal regulations to minimize their impact on the environment.

Uranium, which is likewise a potential contaminant of the environment, is also mobilized in chemical processing of phosphate rock and finds its way principally into liquid and solid wastes. Both fluorine and uranium are recoverable as byproducts in chemical processing of phosphate ores. Uranium recovery, in particular, is becoming economically attractive, and some phosphoric acid producers have begun to recover byproduct uranium. Other producers are constructing facilities for this purpose. The phosphate industry could become a significant source of uranium supply in the future. Other accessory elements, such as the rare earths, vanadium, and others, are recoverable. At current prices, there is little economic incentive to separate these constituents.

Redistribution of accessory elements and compounds can occur at all stages of exploiting phosphate resources, including mining of ores, beneficiation, rock drying, rock transportation, waste disposal, chemical processing, and even the application of fertilizer products to the soils. The basic technology to control potential environmental hazards is known. Regulations are in effect to minimize environmental problems.

Alumina

The United States presently depends almost entirely on foreign sources for its aluminum supply. However, increasing costs of bauxite from traditional overseas sources and growing instabilities in the international market should encourage the United States to consider the potential of various domestic sources. The United States has extremely limited resources of bauxite, the conventionally used source of aluminum. However, it has large quantities of non-bauxitic aluminum resources. The most attractive of these as potential sources of aluminum are high-alumina clays and alunite deposits. Lesser interest attaches to dawsonite in oil shales, anorthosites, and nepheline syenites. The redistribution of accessory constituents in any processing for recovery of alumina would depend on the type of material used as mill feed and the specific recovery process used.

High-alumina clays are composed largely of kaolin and contain over 30 percent alumina. The principal deposits, totalling more than 9 billion tons, are in Georgia and South Carolina. They are amenable to open-pit mining and can be processed by several different methods. Some impurities are present, but very few that might cause environmental problems. Most of the liquid, solid and gaseous wastes can be controlled by known techniques. There could be some potential for byproduct recovery though the economics of byproduct production are not attractive at present. The current mining of clays and disposal of waste products are carried out under state-controlled environmental standards and procedures and no serious environmental problems are envisioned.

Alunite occurs in vein and bedded sedimentary deposits and as disseminated aggregates in igneous rocks. Vein and bedded deposits rarely exceed 1 million tons in size and are not likely to be sources of alumina in the foreseeable future. But disseminated deposits are very large, up to 100 million tons. Those containing 25 to 30 percent alunite are the most promising as potential sources of alumina. But alunite mineralization is erratic in many deposits and only a few ore bodies occur with sufficient consistency of mineralization to be exploitable. Any mining of alunite deposits would most likely be done using surface-mining methods, and involve drilling and blasting of the generally hard rock. Large volumes of material would be moved and disposal of wastes might be a problem depending on the site and disposal plan. Wastes from mining consist primarily of overburden and waste rock associated with the alunite ore. Oxidation and leaching of pyrite in spoil piles could occur and sulfuric acid and soluble ferric sulfates produced. These could become environmental contaminants.

Either caustic-leach or acid-leach processes may be used to treat the alunite. Both processes produce potassium sulfate as a coproduct. Sulfuric acid also can be recovered as a byproduct from caustic-leach processes. There may be some potential for byproduct recovery of vanadium, gallium, and other metals associated with alunite deposits, but to date there has been little interest in this.

The Alumet caustic-leach process for treating alunite results in wastes that are composed largely of silica. These can be slurried to tailing ponds for disposal. The Alumet plant plans to process phosphate rock with sulfuric acid generated in producing alumina, and this could result in the production of contaminants discussed earlier. Ore roasting will produce varying amounts of sulfur dioxide and particulate emissions.

Acid-alumina-leach processes may solubilize some elements not taken into solution by caustic leach, but insufficient data are in hand to characterize the accessory constituents or assess possible environmental impacts.

Dawsonite, an aluminum-bearing carbonate, makes up about 10 percent of the oil shales over a large part of the Piceance Creek Basin in Colorado. In places the rocks contain as much as 3 weight percent extractable alumina and are a potential source of aluminum. The most likely method of recovering alumina would be the leaching of retorted oil shale with a mild caustic solution. The recovery of alumina might well be undertaken in conjunction with oil recovery and hence have the same set of problems relating to the redistribution of accessory elements. Oil shale retort waters are known to have high concentrations of uranium, arsenic, tin, fluorine, iron, and boron, and similar concentrations might be expected in process waters used in recovery of alumina. However, there is little detailed information on the mobilization and fate of accessory elements in the several processes proposed for alumina recovery. Byproduct potential would probably be similar to that of processing oil shales for oil, with soda ash a principal byproduct consideration. Disposal of waste rock would be a major environmental concern.

Anorthosite is an igneous rock characterized by a relatively high alumina content, ranging from 25 to 30 percent. It is not likely to be mined in the foreseeable future. Anorthosites occur in several localities in the United States, with the best known occurring in the Adirondacks. The major anorthosite bodies are igneous intrusions that occupy areas as large as 1,000 square miles. Resources are estimated to be in the billions of tons. Few accessory elements are present in anorthosites in significant amounts and none are presently known to have any economic or environmental importance.

If anorthosite bodies were to be mined, open-pit methods would be used. Large volumes of material would be moved and there might be problems of blowing dust. There might also be a problem with leaching of waste piles, particularly the sintered and leached products from which the alumina had been extracted, although little information is currently available on the behavior of accessory elements during sintering and subsequent leaching.

Nepheline syenites are coarsely crystalline igneous rocks occurring in small intrusive masses rarely exceeding a few square miles in extent. They contain alumina ranging in concentrations from 17 to 23 percent. A number of associated accessory elements are present in amounts 5 to 10 times greater than their crustal abundances, but only cerium, lanthanum and niobium might have some economic significance.

Like anorthosites, the nepheline syenites, if mined, would involve open-pit methods to remove large volumes of rock that would be treated by sintering/leaching processes. Intensive leaching could lead to increased alkalinity of surface runoff. However, there is very little detailed information on the mineralogy, accessory element content, and tonnages of nepheline syenite deposits or on their suitability for alumina production. The small size of nepheline syenite deposits and their relatively low content of alumina make it unlikely that they will be developed for alumina in the United States in the foreseeable future.

CENTRAL FINDINGS AND OBSERVATIONS

Availability of Data

Coal

Data on the distributions and concentrations of some accessory elements in coals from different areas are extensive. However, because coal reserves are present in billions of tons and because wide variances exist in the distributions of accessory elements, information on which to base an assessment of accessory element redistribution or byproduct potential must be considered inadequate. The data base is insufficient to predict accurately the mean concentrations or the range of elements in the coals of different coal basins or even of individual beds. However, we do have a fairly broad view of the kinds and amounts of accessory elements in U.S. coals, and for some areas, such as the Illinois Basin, the data are rather comprehensive. For many areas, suites of accessory elements can be consistently identified in certain coals, and for some major coal seams, patterns of occurrence are beginning to emerge. Because values reported for accessory elements in various coals come from limited samples and may differ by 1 or 2 orders of magnitude, it is unlikely that reported concentrations of a particular element in a whole coal will be representative of that coal. An accurate representative chemistry is important in characterizing a coal for a particular use and for considering the potential for byproduct recovery of certain elements.

Knowledge of the physical and chemical characteristics of accessory elements in coal-cleaning wastes is likewise limited and inadequate to assess refuse disposal problems, such as ground-water pollution, or to assess the potential for byproduct recovery. Nor, except for sulfur, is it possible to quantify the relationship between raw-coal and clean-coal analyses. For coal-conversion-plant emissions there are inadequate data on the distribution of many trace elements, and organic emissions from coal conversion are largely uncharacterized. Furthermore, the amount of data is limited on the concentrations and solubilities of accessory elements in ash and sludge that might be disposed of in underground mines, strip-mined areas, or landfills that are subsequently buried.

Much information is available on different aspects of coal mining, beneficiation, burning, and treatment of wastes, but the total amount of data is sparse relative to the magnitude of the resource and requirements for future use. Until a broader data base is available, it will not be possible to predict with reasonable assurance the commercial future of recovering accessory elements or the total environmental impact of coal utilization.

If the problems of future large-scale mining of coal are to be adequately addressed our fundamental geologic and chemical knowledge of coal will need to be greatly expanded. In addition, the complex interactions of accessory elements and compounds during beneficiation, burning, and waste disposal will need intensive study. Of special importance are studies of the composition and disposition of wastes, effluents, and emissions associated with coal-conversion processes. These processes, inadequately understood at present, are likely to become highly significant in future exploitation of coal resources. Baseline studies should be made now so that future coal-conversion problems will not suddenly appear without a sound basis for resolution.

Oil Shale

There is presently no commercial production of oil from oil shale and no history of commercial production from which data on the redistribution of accessory elements from oil shales can be obtained. Information on the composition and behavior of accessory constituents in oil shales comes from fundamental scientific and engineering studies made over the years, and recent pilot- and demonstration-plant operations. There are more chemical and mineralogical data on the raw shale and surface waters than on products of processing or on ground waters associated with oil shale regions. Information is now being developed on the composition of process water, retorted shale, leachates, and stack gases as well as the possible impact on the terrestrial environment, and surface and ground waters. However, there is as yet an insufficient understanding of mechanisms and pathways of redistribution of accessory elements for environmentally sound planning and management of large-scale mining and processing operations. To develop this understanding will require continued and expanded efforts to characterize the chemical and physical nature of process-stream materials that may reach the environment as a result of oil shale extraction processes. These efforts in turn should be coupled with studies of atmospheric and hydrologic transport of accessory constituents. Basic atmospheric and hydrologic data and transport models are needed to assess the impact of gaseous effluents on flora and fauna, water use and movement, and the mobility and effects of salts, trace metals, and trace organics in surface and ground waters. For predictive purposes it is essential that the basic inventory and interactions among accessory elements and compounds at all stages of mining, beneficiation, chemical processing, and waste disposal be broadened to include principal technologies and time-dependent changes. This will require not only intensive laboratory investigations but also full-scale process demonstrations as well as monitoring of waste effluent movements.

Uranium

Except for the Colorado Plateau ores there is relatively little information on the concentrations and distributions of accessory elements in uranium ores. Even for the Colorado Plateau deposits, for which abundant information exists in the literature, the data are incomplete and pertain mostly to hand specimens of a few hundred grams. These data are not reflected in the concentrations of ore shipped to mills. The reason is that accessory elements are erratically distributed within deposits and concentrated either in organic-rich pockets, in discrete sedimentary beds, or secondary structures ("rolls"). Ore is homogenized in mining and milling, and the range of concentrations in mill feed and concentrate reduced from its original broad span. Available accessory element data therefore reflect average concentrations within large volumes of ore.

The only consistent data are from Colorado Plateau ores mined in the 1950s, but they suffer because older analytical methods were not as accurate as those used today. Also, in earlier mined ores no analyses were made for certain elements that are routinely determined today. Furthermore, no analyses of accessory element concentrations were made of uranium ores from Wyoming, Texas or New Mexico. However, the U.S. Geological Survey and a number of State Surveys are now beginning to collect and evaluate accessory element data from current production and potentially commercial sites.

Phosphates

Geological and geochemical data on phosphates have accumulated over many years, primarily with the development of the fertilizer industry, and our information base today is extensive. Except for probable offshore deposits, our domestic phosphate resources are well known. The chemical compositions, mineralogical forms, and structural properties of phosphates have been extensively studied and are well documented. More importantly, the behavior of various elements and compounds in chemical processing for fertilizer production is, with some exceptions, well known, thus providing a firm base for dealing with many potential environmental impacts. However, specific problems, such as ground-water contamination, need further study to document the geochemical pathways of accesory elements and compounds into the environment. We do not yet have sufficient detail on radon emissions from spoil piles. Nor do we have complete understanding of the impact of fluorine emissions from processing-plant cooling-pond waters. Additional data are needed on the long-term cumulative effects of fertilizer application to farm soils and on the plant uptake of trace elements. Finally, if phosphate ores are used extensively in the future for their uranium content, it will be necessary to develop additional data on removal of certain constituents from ores and to investigate chemical pathways through which contaminants might escape into the environment.

It will also be important to further develop or improve methods for economic mining and processing of phosphate deposits that are deeper and lower grade than those being mined today. Future studies should not only seek efficient means for physically removing the deeper deposits from the ground but also improved ways of beneficiating low-grade ores. It will be especially important to seek ways to minimize the use of water. With decreasing grade of ore it would also seem desirable to investigate further the economic recovery of byproduct constituents. Waste disposal and land reclamation will continue to be major problems requiring continued research. Improved methodology for waste disposal should also involve ways of recovering phosphates lost to slimes.

Alumina

There is presently no commercial production of alumina in the United States from high-alumina clays, alunite, dawsonite, anorthosite or nepheline syenite. Basic data on concentrations of specific accessory elements in these deposits are limited and are known primarily from general studies or from investigations involving other commodity extraction potential. Thus, a good deal of information is available on southeastern U.S. clays which are presently processed for their use in paper manufacture and related commercial applications. However, more pilot-plant information on processing of clays for their alumina content is needed before a rigorous assessment of potential environmental problems can be made.

Alunite deposits have been studied fairly extensively, especially those in Utah, and the kinds of accessory constituents are reasonably well known and their potential distributions in nature have been estimated. In addition, all of the mining and waste disposal techniques necessary for alunite mining are well developed in other sectors of the mining industry and most of the technology to be used in processing has already been well established in other metallurgical applications.

What is known of dawsonite associations comes from early basic studies of the oil shales and more recent investigations specifically related to recovery of oil from those rocks. However, the mineral and organic hosts of most trace elements, their stratigraphic distributions, and associations of accessory constituents in dawsonitic oil shale are still poorly known. Furthermore, almost nothing is known about the mobilization and fate of accessory elements in the several processes proposed for alumina recovery. Studies should be made of the mass balance, transport, and fate of accessory elements not only in processing but also in disposal of retorted shale wastes.

Basic mineralogical data are available for the anorthosites and nepheline syenites, but very little information exists on the accessory element content of these rocks. Complete chemical analyses of representative samples of anorthosites and nepheline syenites are not available in sufficient quantity to permit an adequate review of the potential for redistribution and byproduct recovery of accessory elements. Data are particularly lacking on the behavior of accessory elements during sintering and subsequent leaching operations that would be used in recovering alumina from these rocks.

If non-bauxitic resources are to be used as a source of alumina the behavior of accessory elements during processing and disposal of wastes will need to be understood. With few exceptions one can only speculate today about the redistribution and behavior of accessory elements in the mining and processing of non-bauxitic materials.

Environmental Impact of Redistribution

Coal

A wide variety of accessory elements is found in coal and the potential for redistribution of accessory elements and compounds into the environment at all stages of mining, beneficiation, burning, and disposal of wastes is large. Coal mining has been an important cause of redistribution of accessory elements in the Appalachian and Eastern Interior Coal Regions. If strip-mined areas are left untreated, the redistributed overburden can become extremely acid due to the weathering of pyrite and subsequent leaching of the spoil piles. Where spoils are used to backfill a mine, highly mineralized leachates may develop and percolate into the ground-water system. The drainage from both strip and underground mines can be highly acidic, and where mines have been abandoned this drainage is the greatest single source of acid mine water and probably the most difficult environmental impact to control. Acid mine drainage is not a significant problem with most western coals because they contain very little pyrite.

Effective coal-cleaning processes have been developed for removing many of the contaminants from coals, but there still remains a significant potential for environmental pollution. Many contaminants still find their way into combustion wastes. Both the solid and gaseous wastes from power plants pose a particular concern. It is obvious, though, that cleaning up one source of waste, such as stack gases, transfers the contamination problem elsewhere, as in the wet sludges resulting from flue-gas desulfurization. Thus, the environmental tradeoffs of different disposal streams need careful analysis. Despite the recovery system employed, some level of contaminants, such as arsenic, selenium, sulfur, fluorine, and mercury, pass through the stacks of present coal-fired power plants. Some two dozen elements are of concern.

Elements escaping into the atmosphere affect the surrounding vegetation, with the most severe impacts confined to relatively short distances from the power plant. The severity of injury resulting from gaseous emissions can be very great from either acute or chronic air pollution conditions. Of the trace elements that are emitted, many are associated with fly-ash particles too small to be effectively trapped using conventional scrubber and precipitation equipment. Some are emitted mainly in the gaseous state, particularly the oxides of sulfur, nitrogen, and carbon. Selenium, mercury, antimony, arsenic, cadmium, and molybdenum, as well as fluorine, may also escape in this manner. However, new techniques (fabric filtration, baghouse temperature control) in combination with conventional stack-gas scrubbing may provide a measure of increased control for particulate and gaseous emissions.

High-Btu gasification processes carried out under elevated temperatures and pressures produce two major effluents--solid ash and slag, and liquid wastes from scrubbing raw gas. Each of these effluents is a potential conduit for accessory element redistribution.

Increased development of coal-conversion plants could result in the production of large quantities of waste, largely in solid form but with lesser streams of liquid and airborne wastes. Any future large-scale use of conversion plants will require the disposal of vast amounts of wastes that may contain solid chemical compounds not in the original coal. More data are needed to assess the potential for redistribution of elements in different effluent streams and final waste disposal sites under differing conditions.

The proposed underground gasification of coal is likely to pose the same environmental problems as conventional coal extraction techniques.

There may be temporary disruption of the land surface as well as subsidence similar to that resulting from underground coal mining. In situ gasification will also result in the mobilization of accessory elements that could contaminate ground-water supplies. However, there is no good baseline data on element mobilization in subsurface coal-conversion processes. Such data will come only as sites become operational or demonstration projects provide commercial-scale results.

The pH of the enclosing medium is one of the most important factors affecting the solubility of accessory elements in coal solid wastes. Many of these wastes contain sulfide minerals that can oxidize and acidify the water. Acid water in turn may become charged with heavy metals from the solid wastes. Knowledge of coal-ash solubility and methods for environmentally acceptable disposal of coal ash is still incomplete. Laboratory studies indicate that rapid leaching occurs for some accessory elements, but it is not known whether this is restricted just to the surface of the ash deposit or characterizes the full thickness of ash. The disposal of wastes produced from coal-combustion and coal-conversion processes may affect the quality of local surface- and ground-water systems, especially if the disposal areas are subject to seepage or are in proximity to aquifers.

The opportunities for environmental contamination from coal mining, processing, burning, and waste disposal are many. This is implicit in the large number of accessory elements, many of them toxic, found in raw coals and processing wastes. Considered in terms of the tremendously large quantities of coal being mined today and the expectation that more than a billion tons of coal per year may be mined in the not-too-distant future, the potential impact of redistribution of accessory elements into the environment becomes severe. A better and more thorough understanding of redistribution mechanisms and pathways is needed to prevent serious environmental degradation and contamination.

Oil Shale

Due to the wide variety of accessory elements associated with oil shales there is a likelihood that mining and processing would result in redistributions of accessory constituents with potentially adverse environmental impact. The high concentration of fluorine in raw oil shale, for example, and its identification in retorted shale, retorted shale leachates, particulates, and ground waters indicate a particular problem to future mining and processing operations. Natural ground waters in some oil shale areas are already known to exceed public health standards for fluorine as well as other elements, such as arsenic, iron, manganese, mercury, and sulfur. Without special mitigating measures, mining and processing of oil shale could aggravate the problems of ground-water contamination.

Because most of the trace elements in oil shale are retained in the retorted shale after processing, a major adverse environmental impact could result from the redistribution of accessory elements through solubilization and resuspension of retorted shale. Of special concern is the large volume of retorted shale that is expected to be generated in a developed industry, as much as a million or more tons per day. The potential for adverse impacts is increased by the fact that retorted shale has a higher porosity than raw shale. Unless waste-pile surfaces are stabilized, this high porosity, in combination with the vast quantities of waste, might permit profound wind erosion and extensive leaching of accessory elements to ground and surface waters. Among the elements of concern in the retorted shale are arsenic, beryllium, cadmium, chromium, cobalt, fluorine, lead, lithium, manganese, molybdenum, nickel, vanadium, and zinc. The mobility of these elements and organic residues with time is a major unanswered question.

The gases produced during retorting and in scrubber wastes also may contain accessory elements that would be redistributed locally and regionally. Although little information is presently available on the composition of off-gases, it seems likely that fluorine, sulfur, arsenic, and mercury will be present and could pose an environmental hazard.

Limited knowledge of accessory element compositions and redistribution mechanisms and pathways makes it difficult to assess rigorously the environmental impacts of oil shale exploitation. But the potential exists for environmental contamination from mining and processing of oil shale. This must be assessed in research and monitoring programs, and to minimize environmental impacts, precautions will need to be taken at all stages of mining, retorting, and waste disposal.

Uranium

The potential escape of radioactive elements to the environment is the principal concern in considering the redistribution of accessory constituents in uranium ores. The average radium content of measured tailings is 700 picocuries per gram, about the same as feed ore. But after mining and milling, radionuclides are more accessible to plants and animals because of exposure of finely ground tailings on surfaces of waste dumps. Exposure can come from wind-blown dust carrying thorium-232 and radium-226, inhalation of radon-222 (radon gas), gamma radiation, or contamination of ground waters. Stabilization of tailings is therefore required. A tailings cover of clay of about 5 feet can attenuate the exposure by an estimated 80 percent. The disposition of tailings is a problem that will increase with expanded mining and milling of uranium ores. The nature of the problem will not change but the the magnitude will. Health effects can be estimated in terms of curie exposure and the population at risk.

Control and management of tailings piles were inadequate at some uranium mills in the past. An EPA survey of 20 inactive mills found excessive radiation within short distances of old tailings piles. Dispersion was due to wind. Some old tailings piles have contaminated streams with radium-226, as well as selenium and vanadium, to the extent that water quality does not meet standards for irrigation or livestock watering.

Phosphates

A number of accessory elements are mobilized in the mining and processing of phosphate ores but two, namely fluorine and uranium, have possible deleterious impacts on the environment and are thus of special concern. During mining, uranium and fluorine contained in the phosphate rock matrix are generally not mobilized, except in the form of airborne particulate emissions. But uranium-decay products do occur in spoil piles where leach-zone rock and overburden are commingled in mining operations, and where there is a potential emanation of radon gas. Mine waste water, which may be discharged into surrounding streams, is a potential escape route of undesirable elements into the environment, but generally these waste waters are cleaned before discharge, as required by state and EPA regulations. Most of the uranium losses occur in the slimes and sand tailings and are of concern because they are commonly used in land reclamation. These wastes can be isolated by capping with a sufficient thickness of overburden, which helps reduce surface radon emanations, but in older mining areas, where clay slimes were merely discarded, the presence of uranium and other radioactive materials near the surface may be an environmental hazard.

The chemical processing of phosphate ores offers the greatest potential for redistribution of accessory elements and compounds. Acidulation processes completely dissolve the apatite host minerals, and accessory elements and compounds are mobilized. Fluorine finds its way into stack emissions, process water, and waste products. Emission standards require the scrubbing of stack gases to minimize fluorine escape into the atmosphere. Yet, some leakage into the environment still occurs. Process water likewise contains fluorine and must be controlled to prevent loss of fluorine into the surrounding subsurface-water environment. Solid fluorides in waste products are generally contained within the processing and storage-pond systems, although storage-pond water does provide an escape route for fluorine emissions to the atmosphere. If pond waters must be released they are first treated to meet EPA standards so as to minimize any potential contamination of surface and ground waters.

Most of the heavy metals found in phosphate ores are retained in wet-process phosphate fertilizers and eventually find their way into the soils, where they may be absorbed by soil minerals, taken up by plants or leached into surface or ground waters. However, the concentrations of heavy metals in fertilizers are very low and may not result in any increased concentration in plants. The uptake of uranium and radium contained in fertilizers is likewise believed to be low but worthy of mention for environmental monitoring.

Alumina

Because the data base on accessory elements in non-bauxitic materials is so limited it is not possible to provide a confident assessment of the potential environmental impact of mining and processing activities. However, some data are available. In the Alumet process for treating alunite the slurry water is known to be mildly alkaline, but will not contain significant concentrations of heavy metals or toxicants in solution. But off-gases from roasting of the alunite ore, if not cleaned, might contain enough sulfur dioxide and particulate emissions to cause some environmental degradation. There might also be some leaching of pyrite from alunite waste piles.

In any processing of dawsonitic shales for alumina it can be expected that accessory element redistribution problems will be essentially those of processing oil shales for their oil content. There will be large volumes of waste to be disposed of which might be leached of accessory constituents such as arsenic, fluorine and certain sulfides, and in turn contaminate ground-water supplies. Blowing dust from fine particles in waste piles could also be a problem. In addition, arsenic, fluorine and other elements might accumulate in retort waters and find their way into the environment.

Anorthosites and nepheline syenites are not mined in the United States today for their alumina content and little is known about the possible fate of accessory elements in any processing scheme. There are extremely limited data on which to base any assessment of the environmental impact of mining and processing. However, should these rocks be processed for alumina, there could be some redistribution of elements as a result of sintering, leaching, desilication, calcination, and evaporation. Not enough is known at present to predict what redistributions of accessory elements might occur.

Potential for Byproduct Recovery

Coal

The potential for byproduct recovery of accessory elements found in coals would appear to be substantial. By virtue of the large volumes of coal that are processed and burned, the quantities of accessory elements that might be recovered become significant, even though the elements may occur only in minor or trace amounts in the raw coal. Some coal-processing wastes may contain more than 2.5 times the trace-element concentration of the raw coal and could provide feed for subsequent upgrading and possible recovery. The economic recovery of accessory elements from coal-preparation-plant refuse is improved to the extent the production of the coal has borne the total mining and initial preparation costs. As market prices rise the refuse from fine-cleaning may warrant special attention for recovery of accessory elements. Additional crushing would not be necessary and, in general, traditional concentration and separation techniques could be employed to produce a final product. Alternatively, leaching might permit the recovery of heavy-metal ions from coal-preparation wastes by hydrometallurgical techniques, such as precipitation, adsorption, ion exchange and solvent extraction.

Ash and combustion wastes from coal-fired power plants and the wastes resulting from coal-conversion processes all contain significant quantities of accessory elements and might have some potential for byproduct recovery. However, data are presently insufficient to make other than speculative judgments about this potential.

Oil Shale

The opportunities for recovering byproducts in the processing of oil shale are difficult to assess due to the paucity of basic data on form, concentration, and process for potential product development. The most attractive opportunities lie in the recovery of aluminum from dawsonite and soda ash from nahcolite. These accessory minerals are widely associated with oil shale in the Piceance Creek Basin and might be economically recovered in large-scale oil shale operations.

Uranium

Byproduct elements associated with uranium ores all have sources of supply much greater than that involved with production of uranium oxide. Accessory elements in uranium ores are incidental and are of economic importance only insofar as they affect the cost of a particular operation. However, there is a potential for recovery of certain elements. Some Utah and Arizona uranium ores contain .15 to 2.0 percent copper and trace amounts of silver. The copper can be recovered by flotation of sulfides and concentration of solubilized copper from effluents from uranium ion-exchange or solvent-extraction processes.

Molybdenum can be recovered and has been marketed in limited amounts as a calcium molybdate or ammonium phosphomolybdenate containing 40 to 50 percent molybdenum. Recovery of molybdenum is significant only as an environmental or purity consideration. Other elements, such as rhenium, scandium, selenium, thorium-232, and vanadium, could be recovered but there is no economic incentive to do so at this time.

Phosphate

Byproduct production of accessory elements in phosphate chemical plants has been limited by virtue of the costliness of recovery methods. Even though certain metals and rare earths are in solution in the phosphoric acid process it has not been economic to recover them. However, the large volumes of phosphates treated annually in fertilizer manufacture might make byproduct recovery feasible for some elements, for example, the rare earths. Fluorine, which is present in significant quantities in the production of phosphoric acid, must be controlled to meet EPA emission standards. It can be readily recovered as a byproduct of phosphoric acid and elemental phosphorus production but at present there is no economic incentive to do so.

Of greater attractiveness today is the potential for byproduct recovery of uranium, which is present in phosphate ores in amounts averaging .01 percent. Despite this trace amount of uranium in phosphate ores, the total quantities of phosphoric acid produced each year, together with increasing prices for uranium oxide, make uranium recovery of economic interest. Some large phosphoric acid producers currently recover byproduct uranium and several others have announced their intentions of constructing facilities to recover this byproduct uranium. Uranium might also be recovered in the production of elemental phosphorus. The projections of the U.S. Department of Energy (DOE) and others suggest than as much as 4,000 tons or more of uranium oxide will be recovered each year by the phosphate industry.

Of lesser interest is the byproduct potential in the production of elemental phosphorus. Slag from phosphorus furnaces has some potential as an aggregate material. Ferrophosphorus is at present a commercially viable though limited byproduct from the production of elemental phosphorus, and some precipitator dust has been sold as a byproduct for its phosphorus pentoxide and potash fertilizer values. Vanadium, chromium, germanium, and gallium may have some very limited potential as byproducts of elemental phosphorus production, but there is little economic incentive to recover these products at present.

Alumina

The potential for byproduct recovery of elements associated with processing alumina ores is not very high. Silica from the treating of high-alumina clays might be recovered and find use as a filler for newsprint and rubber, and if the titania content could be concentrated it might be a source of pigment-grade titanium oxide.

Potassium sulfate is a probable coproduct of the Alumet process in treating alunite ores and the production of sulfuric acid is a potential byproduct of all the schemes considered in processing alunite. In any processing of dawsonitic oil shales for alumina it is likely that nahcolite would be recovered as a coproduct for the production of soda ash. Retorted shale might have some potential use in lightweight aggregates, portland cement, brick, road construction materials, and glass and glass ceramics. Potassium could be a potential byproduct of processing anorthosites, and both sodium and potassium byproducts of nepheline syenites. However, there is at present no incentive to recover byproducts from non-bauxitic rocks and the potential for byproduct recovery is discussed only insofar as large-scale mining and processing might be undertaken at some future date and make byproduct recovery possible.

Technological Impact on Future Mining and Processing

Coal

The technologies in use today are expected by industry to remain in use for many years in the mining and processing of much of our coal output. The scale of individual surface-mining operations in western coal seams may be nearing a peak. No radically new types of equipment are under development. This does not imply that mining technology is satisfactory. No mechanical mining methods are available for the thick deep seams which will have to be extracted by underground-mining methods. Until such systems are devised it is uncertain how future accessory element redistribution from such deposits will be affected.

Strip-mining practices in both western and eastern deposits will be changed by the Surface Mining Control and Reclamation Act of 1977. Enforcement of the Act should result in a reduction of the impacts of accessory element redistribution per ton of coal mined, since it disqualifies from mining certain types of deposits where environmental impacts are difficult or nearly impossible to control economically.

Underground mining in the eastern thinner seam deposits will require new mining systems and equipment in order to help reverse the decline in productivity that has occurred in the past 10 years. Such systems have not yet been developed. Attempts to introduce longwall mining in place of room-and-pillar methods have met with limited success. On balance, it is not likely that new problems associated with accessory element redistribution, other than those resulting from increased production, will arise.

In the processing of mined coal, one can expect an increase in the amount of coal that is beneficiated in order to reduce emission of pollutants during utilization. This will result in production of increased quantities of solid wastes per ton mined, from which the escape of accessory elements must be prevented. New higher-cost and more efficient technologies for beneficiation may be developed but existing processes will probably continue to dominate the industry for many years.

Direct coal combustion will continue to be the major use for coal for at least the next 20 years. If national energy policies are implemented to the degree contemplated, the combustion of coal will more than double in the next 10 years. Requirements to prevent environmental contamination will almost surely result in attempts to improve coal-cleaning processes, coal-burning systems, and disposal of wastes, and these in turn will affect the redistribution of accessory constituents. For example, control of sulfur oxides by using stack scrubbers and throwaway lime or limestone processes will create very large tonnages of solid wastes, from which the potential for accessory element redistribution into the biosphere is very great. Alternatively, sulfur oxide control might be achieved by the use of fluid-bed combustion but this also creates a new set of problems with respect to environmental controls and possible accessory element redistribution.

Coal-conversion processes to convert coal to liquid or gaseous fuels, once they become commercial, will affect the redistribution of accessory elements and compounds. These processes create solid, liquid, and gaseous residues that are chemically different from those that are generated by direct combustion and will generally require different environmental control practices, if redistribution of accessory elements is to be minimized. The exact chemical nature of these substances and methods required to prevent their dissemination into the environment will not be known until we have had, at the very least, substantial experience with pilot-plant design and operation.

In situ coal gasification presents some unique technical environmental problems and possibly increases the mobility of accessory elements at considerable depths in the earth. Ground waters could become enriched and perhaps polluted with certain elements. But one can only speculate about the changes that might occur since there is no information on the special environmental problems and effects that will be created by *in situ* gasification, a process that takes place under conditions that are extremely difficult to control and are highly site-specific.

Oil Shale

A number of different above- and belowground processes have been developed or are being developed to extract oil from oil shale, but the accessory element contents of products and residuals as a function of technology type and process variables are only now becoming available. It is thus possible to assess the relationships of technology to the redistribution of accessory elements only in a general way. General distributions of accessory elements can be predicted but the mechanisms and pathways of redistribution need to be better understood. Aboveground retorting is now quite refined but belowground retorting remains under development.

Uranium

Substantial changes in extractive metallurgical processing of uranium ores are not likely in the next 25 years, especially changes that might affect the production of accessory elements or cause environmental concerns. A possible exception is in situ leaching of uranium ores, which will cause mobilization and possible escape of uranium and some associated elements from the leach field. Present knowledge of the fate of accessory elements and compounds in the in situ leaching of uranium ores is poorly known.

Except for radioactive constituents, there is some similarity in the accessory element content of uranium and copper ores. The wide technological base for processing copper ores suggests that environmental concerns and possible byproduct production as uranium mining increases should pose no new questions.

Phosphates

It is likely that the production of phosphates over the next 25 years will use existing mining, beneficiation, and processing technologies, and in general no major new problems in the redistribution of accessory elements and compounds should arise. Exceptions to this might develop if new technologies are devised to recover offshore phosphate deposits. Any new technology could spawn new problems in the redistribution of accessory elements and compounds. Processes for recovery of uranium from phosphate ores are well developed. However, sustained production of byproduct uranium could result in new technical requirements, waste products, and conditions of disposal that could bring additional problems of redistribution.

Alumina

The technological impact of processing non-bauxitic sources of alumina can be assessed only in a speculative way in the absence of any commercial production from these sources. Acid processing of high-alumina clays has been tested in pilot plants and some information is available on the fate of accessory elements mobilized in these operations. Alunite has been processed commercially in other countries for its alumina content and some data are available on the effects of caustic-leach and acid-leach processes on the redistribution of accessory elements.

Techniques for processing dawsonitic oil shales have been developed but it is too early to evaluate the effects of these techniques, either in assessing byproduct recovery potential or environmental impact of redistributing accessory elements. Virtually nothing is known about processing anorthosites and nepheline syenites other than the probable use of sintering and leaching methods as a basis for recovering alumina. If non-bauxitic aluminum resources are exploited in the future it is likely that some new processing technologies may be required, but at present no new methods of treating these materials are known to be under development.

REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS FROM MINING AND PROCESSING OF URANIUM ORES

SUMMARY

The Uranium Panel of the Committee on Accessory Elements has studied the probable impact on the economy and environment of the increased production of accessory elements as the tonnage of uranium ore being mined and milled increases over the span of the next 25 years. Consideration has been given to the possibility of production of uranium from new sources, changes in environmental constraints, and different processing methods.

The following conclusions were drawn from the study:

1. By 1985 it is estimated that the uranium industry may be milling as much as 85,000 short tons of ore per day averaging .10 percent U_3O_8. There may be twice this amount by the year 2000. Most of this ore will be of the sandstone type comparable to currently milled ores but of lower grade.

2. As far as production of specific accessory elements is concerned, the current mining of sandstone-type deposits can be expected to continue with the only change being an increased production commensurate with larger-scale operations in the future.

3. Tailings from milling of uranium ores contain radioactive materials, and in some past operations these tailings were not adequately contained. The need for proper disposal of tailings will continue to be of vital concern as the scale of mining operations increases, but the nature of the problem will not change with increased tonnage.

Just as tailings management will demand more attention as the scope of operations increases, so will the placement of the spoil from open-pit mining. Covering the spoil piles with topsoil and reseeding or refilling mined-out pits seem to be the acceptable methods.

4. Substantial changes in extractive metallurgical processing do not appear likely in the next 25 years, particularly changes that will affect the production of accessory elements or environmental concerns caused by them. A possible exception in this regard is the development of in situ leaching processes.

The most complete analytical data on the accessory elements contained in the typical sandstone ores are derived from rather extensive sampling of mill pulps from the Colorado Plateau. It is strongly recommended that a sample program similar to that on the Plateau be undertaken from at least one operating mill in each of the uranium-producing districts of the United States.

Because the forecast of future uranium production and the availability of uranium reserves in the United States are so dependent upon U.S. Department of Energy (DOE) projections, it is strongly recommended that the basis of reserve classification by DOE be closely examined.

The normal licensing process will demand greater management control of tailings from uranium mills in the future. However, it is recommended that guidelines be established to set maximum permissible levels for radon emanating from tailings.

ANTICIPATED U_3O_8 REQUIREMENTS FOR THE UNITED STATES

Any consideration of the impact of accessory elements on economic or environmental circumstances will obviously be dependent upon the magnitude of the mining operations in the future. This in turn depends on the requirements for uranium in nuclear reactors, the grade of ore anticipated, the kind of material serving as a source, and the processing methods. Of those factors influencing the accessory element question, the estimate of future uranium requirements has probably received the most attention in the literature.

Uranium Milling Demand Forecast

The lack of any definitive federal energy program at this time makes the forecasting of uranium needs for nuclear power generation very difficult. Further complicating a uranium demand forecast is the disruption to the construction schedule of committed plants owing to a variety of factors, some real, some imaginary. As an example, the 1974 U.S. Energy Research Development Administration (ERDA) forecast for uranium was based on a nuclear generating capacity of 250,000 megawatts by 1985. A more recent appraisal of demand based on assumptions of growth of energy consumption--rates of construction of nuclear plants, availability of enrichment facilities, efficiency of enrichment facilities, the general economy and availability of capital--suggest a considerable slippage in growth. Agency projections, now carried only to 1990, show a demand of 185,000 megawatts by the year 1990 (U.S. DOE 1978a).

All estimates of future uranium requirements, however, call for production rates significantly higher than historic levels. This study, which considers the impact of the accessory elements associated with uranium production, draws on the more generally accepted nuclear power forecasts and determines the necessary uranium-mining and milling capacity to meet those demands. Table 3.1 summarizes the 1978 DOE nuclear power forecast and U_3O_8 requirements through 1990. The uranium requirement assumes no reprocessing of spent fuel discharged from domestic power reactors. It has been further assumed that enrichment tails will contain .20 percent fissionable uranium remaining in the UP_6.

This study has not been concerned with the availability of uranium reserves necessary to meet the requirements noted above nor with the price that might be required to bring about the development of these reserves; it deals only with the impact of accessory elements at the increased mining and milling levels. Certain assumptions relative to ore grade and depth (stripping ratio) are necessary to determine the amount of ore to be milled and the total volume of material to be handled and disposed of. With regard to the former, we have seen a steady decline in the grade of ore milled over the past decade from about .21 to .155 percent U_3O_8. This trend is expected to continue, but it will be countered by increased tonnages of ore mined. This in turn will require handling larger quantities of waste overburden, which is expected to reach 2 to 3 million bank cubic yards per day by 1990.

The lithology of the overburden differs from one mining district to the next. In Wyoming and Texas, for example, the overburden generally consists of sediments of Tertiary age or of Quaternary alluvium. The sediments are mostly interbedded shales, clays, siltstones, mudstone, pebble conglomerates, and arkosic sandstones of variable thickness that were deposited by fresh-water streams and in lakes. The mineralogy of these sediments is usually dependent both on the source rocks from which the sediments were derived and on the types of mineralizing ground-water solutions to which they have been subjected. Generally, the clays and shales have a large amount of volcanic material and may be high in uranium, selenium, and bentonite. Many of the shales have pyrite nodules that were deposited from ground-water solutions high in iron when the sediments were laid down. The sandstones and conglomerates are typical of most arkoses derived from crystalline igneous rocks. They generally have a low quartz content but have a high content of feldspar and clays derived from the feldspars.

In the Colorado Plateau and the Grants, New Mexico, Mineral Belt the overburden sediments are generally much older than those of Wyoming and

TABLE 3.1 U.S. Installed Nuclear Capacity (1978 forecast) and U_3O_8 Requirements

Year	MWe x 1,000	Annual U_3O_8 a/ Requirements (short tons x 1,000)
1980	60	14.8
1985	115	28.3
1990	185	40.4

Note: a/ Assumes 0.20 percent enrichment tails.

SOURCE: Modified from U.S. DOE (1978a).

Texas. The sediments are both marine and nonmarine and are generally Jurassic or Triassic in age, but in some places may be of Tertiary or Quaternary age. These marine sediments include limestones, dolomites, and black shales, as well as high-quartz sands. The mineralogy could be expected to be slightly different, with more carbonate, silicate, and saline minerals being present.

The anticipated milling rate in tons of ore per day will be less by the year 2000 for U_3O_8 production than the milling rate today for copper production. Since there is some similarity of accessory mineral content (except for radioactive constituents) between ores of uranium and of copper, the environmental concerns and byproduct opportunities as uranium mining increases should not pose any new questions for the industry.

Uranium Sources

The total production of uranium from domestic ores through 1977 is reported as 313,100 short tons U_3O_8 (U.S. DOE 1978b). Of this total, about 95 percent was produced from sedimentary deposits (primarily sandstone). The remaining 5 percent was produced from a variety of other host rocks. During 1977 a total of 16,700 tons of U_3O_8 were produced. Fifty percent of this came from underground operations, 46 percent from surface mines, and 4 percent from other sources, such as heap leach, mine waters, and solution mining.

On the basis of our current geologic knowledge it seems likely that sandstone-type deposits will continue to provide the bulk of our domestic uranium production. A recent DOE estimate of reserves, based on a $30 per pound forward price, is reported as 754,000 short tons of U_3O_8 (U.S. DOE 1978b). As noted in Table 3.2, 97 percent of this uranium is in clastic host rock, chiefly sandstone. This in turn suggests that problems relating to accessory elements may be more predictable than if nonsandstone sources of uranium are mined.

In addition to the sandstone deposits it is expected that production of U_3O_8 from unconventional sources will grow significantly, and increasing attention is now being given to byproduct recovery, particularly from phosphate and copper ores. DOE has suggested that byproduct production from wet-phosphoric acid might reach 3,500 tons of U_3O_8 per year by 1985 or 1990 and 6,000 to 9,000 tons of U_3O_8 by the year 2000. Copper leach might provide as much as 500 to 1,000 tons of U_3O_8. DOE has suggested that byproduct sources of uranium through the year 2000 might yield a cumulative total of 140,000 short tons of U_3O_8, 115,000 short tons of which would come from wet-phosphoric acid production and 25,000 short tons from copper dump leach liquid. The National Research Council (1978), however, expects that byproduct uranium production will not exceed 60,000 tons of U_3O_8 through the year 2000. Whatever the total byproduct production from these sources, there is little doubt of its growing importance, and this will require attention to the redistribution of associated accessory elements. Solution mining and heap leaching will also add to the total annual production of U_3O_8 and these, too, will give rise to problems of redistribution of accessory elements. Klemenic's forecast of annual

TABLE 3.2 Distribution of $30 Reserves
(as of 1/1/78) by Type of Host

Host Type	Short tons of ore x 1,000	Percent U_3O_8	Short tons U_3O_8 x 1,000	Percent of total (tons U_3O_8
Coarse Clastics (sandstones)	715,800	0.09	659.3	97
Fine Clastics (shales)	15,100	0.06	9.5	
Lignitic Materials	2,100	0.12	2.5	3
Limestone	900	0.11	1.0	
Igneous and Metamorphic Rocks	20,100	0.09	17.7	
Total	754,000	0.09a/	690.0	100

Note: a/ Average grade.

SOURCE: Modified from U.S. DOE (1978b).

uranium production from unconventional sources is summarized in Table 3.3.

ACCESSORY ELEMENTS IN URANIUM ORES

Most current production of uranium is from sandstone-type deposits, and industry and government scientists and engineers believe that this will continue for several decades. It is likely, however, that future production will be from deposits at greater depth and of considerably lower grade (perhaps as low as .02 percent of U_3O_8). The possibility of discovering significant deposits of other than the sandstone type and the potential for extracting uranium as a byproduct from other ores have been considered, but neither of these alternatives offers much hope of surpassing the sandstone-type deposits in importance in the foreseeable future. Some of the possible alternatives to sandstone-type deposits have been discussed by Armstrong (1975). These include possible byproduct production from phosphate rock, porphyry copper deposits, and lignite. Other types of deposits that could possibly be discovered in the United States are veins, veinlets and disseminations in granite, disseminations in alkalic igneous rocks, and uranium porphyries. Types unlikely to be discovered in the United States in exploitable amounts include uraniferous quartz-pebble conglomerates, calcite-cemented alluvium (calcrete deposits), pegmatites, and black shales. Although uraniferous black shales are known in the United States, Armstrong (1975) points out that they are far from being sufficiently uraniferous to be mined in the foreseeable future.

TABLE 3.3 Estimated Production of Uranium from Nonconventional Sources (short tons U_3O_8 × 1,000)

Year	In Situ Leaching		Phosphate		Heap Leach		Copper Byproduct		Total	
	$30 Forward Cost	Industry Trends*	$30 Forward Cost	Industry Trends*	$30 Forward Cost	Industry Trends*	$30 Forward Cost	Industry Trends*	$30 Forward Cost	Industry Trends*
1980	3.1	2.1	1.4	0.9	0.1	0.2	0.2	0.1	4.8	3.3
1985	4.1	3.7	2.1	2.2	0.2	0.0	0.7	0.2	7.1	6.1
1990	4.2	3.7**	3.5	2.2**	0.2	0.1**	0.8	0.3**	8.7	6.2**

*"mid-case" estimates
**1987 estimated production

SOURCE: J. Klemenic, U.S. Department of Energy, personal communication (1978).

The accessory elements encountered in future uranium mining, and their concentrations, will depend on the types of uranium ore mined. Even if new sources are discovered, it cannot be reasonably expected that the associated accessory element suites will be those present in similar types of deposits elsewhere; it is well known, for example, that sandstone-type deposits have a wide range of concentrations of various accessory elements. This makes prediction exceedingly difficult. However, it has been recognized (IAEA 1974) that, even though concentrations vary widely, a particular suite of accessory elements tends to occur with uranium. This was a major conclusion of a committee ("Working Group IV") convened at a symposium of the International Atomic Energy Agency (IAEA) held in 1974 in Athens, Greece. Elements associated with uranium in "many sedimentary and vein deposits" include Se, V, Mo, Fe, Co, Cu, Be, C, and As. To this list we must add all the daughter products from the natural radioactive decay of uranium. Three of the elements in the list above (vanadium, molybdenum and copper) have been recovered as byproducts in the processing of ores from at least some sedimentary-type deposits.

Other elements that occur with uranium in some deposits are Th, Ni, Pb, S, Ag, Zn, and daughter products from the radioactive decay of thorium. The elements that comprise the host rocks for uranium ores are omitted from the lists above because the concentrations present are no greater than those present in common types of rocks and soils.

Concentrations of Accessory Elements in Uranium Ores

Because sandstone-type deposits are expected to be the major source of uranium for the foreseeable future, it may be useful to examine the concentration ranges of accessory elements in this type of deposit. Abundant data are available in the geochemical and geologic literature, but most data pertain to "hand specimens" of a few hundred grams in size and do not reflect the overall concentrations in large tonnages of ore that are shipped to the mills. The reason for this is that the accessory elements are generally erratically distributed within the deposits and are concentrated in organic-rich pockets, in discrete sedimentary beds, and in secondary structures such as "rolls." The ores become homogenized during the mining and milling processes so that the ranges of concentration are considerably reduced, even though the ranges are still quite broad. Geochemical studies by the U.S. Geological Survey during the 1950s employed mill-pulp samples that were split from homogenized ore shipments during the milling process, and the accessory element data on these samples reflect average concentrations within large ore volumes. All of the mill-pulp samples, however, were from uranium ores of the Colorado Plateau, chiefly (but not exclusively) from the Salt Wash Sandstone member of the Morrison Formation and the Moss Back and Shinarump members of the Chinle Sandstone. The ranges of concentrations, from Shoemaker et al. (1959) and Miesch (unpublished data) are shown in Table 3.4.

It is apparent from the concentration ranges given in Table 3.4 that sandstone-type uranium deposits generally contain no higher concentrations of metals than do other kinds of ores currently being mined on large scales. Thus, the only unique environmental problem that

TABLE 3.4 Ranges of Concentration of Accessory Elements in Sandstone-Type Uranium Ores

Element	General Range (weight percent)
Selenium	0.0001 to 0.05
Vanadium	<0.0001 to 2
Molybdenum	<0.001 to 0.1
Iron	0.1 to 10
Cobalt	0.0001 to 0.1
Copper	0.001 to 1
Beryllium	<0.0001 to 0.0005
Arsenic	0.001 to 1
Nickel	0.0001 to 01
Lead	0.001 to 0.1
Silver	<0.00001 to 0.01
Zinc	0.002 to 0.2

SOURCE: Shoemaker et al. (1959); Miesch, unpublished data (1977).

might be expected to be associated with large-scale uranium mining and processing is that due to the presence of radioactive substances. This subject is discussed in another section of this report.

It has been pointed out that realistic data representing the overall concentrations of accessory elements in large tonnages of uranium ore are available only for ores from the Colorado Plateau that were mined during the 1950s. It should also be mentioned that, although the samples were almost ideal for the purpose of this Panel, some of the methods of laboratory analysis that were used were not as accurate, precise, or sensitive as methods currently being used in trace-element laboratories. Also, the samples were not analyzed for some elements that can now be determined routinely. Another notable shortcoming of the data presented above is that they do not necessarily reflect accessory element concentrations in uranium ores being mined extensively in Wyoming, Texas, and New Mexico. For these reasons, it is recommended that a moderate-size program should be initiated to examine accessory elements in mill-pulp samples from deposits currently being mined within the United States. The program should also include the low-grade materials that we might expect to be mining in future years, but the sampling procedures must be designed to yield results compatible with those obtained from mill pulps.

It should be noted that the U.S. Geological Survey and geological surveys of New Mexico, Texas, and Wyoming are beginning to collect and evaluate accessory element data from current production areas and potential commercial sites. These data are especially pertinent where *in situ* processing has evolved as a possible extraction technique because of potential problems with mobilization of such elements.

As far as production of specific accessory minerals is concerned, the present mining of sandstone-type deposits can be expected to continue, with the only change being an increased production commensurate with large-scale operations in the future.

Byproduct Elements Associated with Uranium

Arsenic and Mercury

No attempt has been made to recover arsenic or mercury from uranium ores in the United States, although several vein-type ores have contained arsenic and mercury as sulfides.

In deposits containing high sulfide concentrations, recovery of arsenic and mercury might be worth studying. This has not been done in the United States because most of the uranium ore being processed is sandstone-type ore, which does not contain any significant concentration of arsenic or mercury.

Copper

Some of the uranium ore from Utah and Arizona contains .15 to 2.0 percent copper; at one time, four uranium ore-processing plants recovered copper from copper-uranium ore by flotation of sulfides from the comminuted ore and by cementation of solubilized copper from the effluents from uranium ion exchange or solvent extraction. These operated for only a few days every year because very little copper-uranium ore was received. Today, only one plant still has copper recovery facilities. Ore is set aside in stockpiles until enough is accumulated for processing.

Molybdenum

Molybdenum occurs in at least trace amounts in all domestic uranium ores and some ores contain a few tenths of a percent or more. Although not much study has been devoted to the mineralogy or mode of occurrence of the molybdenum in these ores, it generally is thought that molybdenum is present as a sulfide, sulfate, a hydrated molybdate, or adsorbed on carbonaceous materials or on hydrated iron oxides.

Usually, more molybdenum is extracted by alkaline carbonate than by acid-leaching solutions. In either case, means are available for removing or controlling the molybdenum concentration in solutions. The sulfide concentrate can be acid-leached for uranium and molybdenum recovery, if warranted.

In acid solutions, various molybdenum control or recovery procedures are available, such as sulfide precipitation, adsorption on activated carbon, and purification by partial neutralization. Molybdenum has been recovered in several uranium mills and usually it has been marketed as a calcium molybdate or an ammonium phosphomolybdate containing 40 to 50 percent molybdenum. Total production to date is estimated to be about a thousand tons of molybdenum. A substantial portion of this resulted from the processing of uraniferous lignites which contained almost as much molybdenum as uranium, but which are not a significant source of uranium at present. The quantities of molybdenum are too small to be a market factor and recovery is an environmental and purity consideration only.

Rhenium

Uranium ores containing molybdenum also contain rhenium in amounts from less than .3 to 3 parts per million. In alkaline leaching, most of the molybdenum and rhenium are dissolved along with the uranium and, if it were economically attractive, both metals could be recovered. In acid-leach liquors, the rhenium content ranges from .03 to 1 part per million. About one-half of the rhenium can be removed from the leach liquor by passing it through a bed of activated charcoal, by treating it with ion-exchange resins, or by solvent extraction with secondary or tertiary amines.

Uranium mills that recover byproduct molybdenum have the best prospects of recovering rhenium. Only one mill has recovered rhenium as a perrhenate solution, but others have investigated the possibility.

Uraniferous Chattanooga Shale from Tennessee contains .05 percent molybdenum and about 1 part per million rhenium. Vanadiferous shales from Wyoming also contain about 1 part per million rhenium. Because of the complex mineral assemblage in the shales and the large amount of organic material present, efforts in the laboratory to collect an enriched rhenium product by roasting and collecting the fumes were unsuccessful.

Scandium

Trace amounts of scandium found in most uranium ores dissolve during acid leaching, yielding solutions containing up to 1 milligram Sc_2O_3 per liter.

The U.S. Bureau of Mines Salt Lake City Metallurgy Research Center has developed a solvent extraction process for scandium recovery but the element is not recovered in any present operation.

Selenium

Selenium has long been known to occur in sandstone-type uranium deposits at concentrations from 1 part per million up to .1 percent. The selenium content does not correlate with the content of any other analyzed constituent in the deposits, and some western soils, such as the Pierre, Niobrara, and Mancos shales, contain concentrations of as much as 200 parts per million.

In the Grants Mineral Belt, selenium is found in the native state as gray or red selenium and as ferroselite ($FeSe_2$), and many of the uranium ores in the area will average about .03 percent selenium.

Selenium is leached from some uranium ores in alkaline circuits and, along with molybdenum, it will tend to concentrate in the recirculated solutions. This buildup is usually controlled by bleeding a small portion of the solution to waste and this bleed stream conceivably could be treated to recover selenium and molybdenum by precipitation of selenium as the sulfide.

Thorium-232

At present, no uranium ore now being processed in the United States contains enough thorium to be a problem or to be worth recovering, although some deposits mined in the past contained enough to require some care to prevent contamination of the uranium product. This was accomplished by changing solvent or adding a precipitation step.

Thorium has been recovered as a byproduct or coproduct of uranium in other countries, but the demand for thorium is not great enough to make its recovery attractive at most operations today.

Vanadium

Since 1960 there have been uranium mills in the United States which have recovered vanadium as a coproduct, and production has been a few thousand tons of vanadium (1,000 to 6,000 tons) per year.

It has not been considered economic to recover the small amounts of vanadium present in uranium ore from outside the Uravan Mineral Belt, although two uranium mills have recovered even these small amounts of vanadium. The Mines Development, Incorporated, in South Dakota recovered vanadium from iron slags and with the same circuit recovered vanadium from uranium-plant tailings. The United Nuclear-Homestake Partners in New Mexico precipitates a sodium diuranate concentrate, containing about 3 percent vanadium, which is calcined and quenched to remove the vanadium. The solubilized vanadium is concentrated and sold.

Enough vanadium is available from nonuranium sources so that currently there is no incentive for uranium ore processing plants to recover vanadium unless the mill feed contains an average of more than .2 percent vanadium. In the Grants area of New Mexico, most uranium ores contain only about .05 percent vanadium or less, and in Wyoming the ores contain less than .01 percent vanadium.

RADIOACTIVITY IN TAILINGS FROM URANIUM MINING

The accessory elements that are unique in uranium mining and milling are those associated with radioactive constituents of the ores. Their potential redistribution is the most significant problem in mining and milling operations. Disposal of tailings is a particular problem because the tailings contain about 85 percent of the natural radioactivity.

The average radium content is 700 picocuries per gram, about the same as the feed ore. But after mining and milling, the radionuclides are more accessible to plants and animals because they are exposed on the surface in waste dumps of finely ground tailings. This exposure can come from windblown dust carrying thorium-230 and radium-226, inhalation of radon-222 (radon gas), gamma radiation, or contamination of ground waters. Though the concentrations of radioactivity after mining and milling are no different than when the ore was underground, they are now above ground and stabilization of the tailings in some manner is therefore required.

A study of this problem has been initiated by ERDA using Ford, Bacon and Davis of Salt Lake City, Utah, to provide engineering architect services. Much of this interest was stimulated by the discovery of radioactivity in dwellings in Grand Junction, Colorado, where sand from tailing piles was used for fill and for some of the mortar in the dwellings.

As the scale of uranium mining and milling increases, the need for proper disposal of tailings will continue; the nature of the problem will not change with increased tonnage, but the magnitude will.

Assuming that radon and other daughter products of uranium-238 might be considered accessory elements, it is possible to estimate the total curies and health effects caused by the treatment of some 85,000 short tons per day of uranium ore at an average grade of .10 percent U_3O_8 (the 1985 estimate). Based on the literature, we can expect 85,000 curies radon-222 per year from ores of this grade and quantity, and can anticipate that 99 percent of the total will pass into the tailings and that at least 80 percent will be retained by and within the tailings. Further, an additional 80 percent attenuation is deemed possible by placing a 5-foot cover of clay over the tailings. This reduces the curie total to about 3,400 (20 percent of 20 percent of the original 85,000 curies) for the total 85,000 short tons. If the production were evenly distributed through 85 mills of 1,000 short tons per day capacity each, there would be a possible release of 40 curies per year per facility.

The curie level on the pile would produce about 35 millirems per year dose to the lung, which is extrapolated via the linear, nonthreshold theory to .007 health effects per year. By the time this gas moves a half mile (assuming this will be the nearest resident), the lung dose drops to less than 1 millirem per year or about .0002 health effects per year.

If the 5-foot cover over the tailings were eliminated, approximately 2,800 curies could be produced in the twelfth year, which could be extrapolated to 2.0 health effects per 50 years. This compares to EPA's model uranium figures of 8.5 health effects over 50 years for no cover versus approximately 1.0 for an equivalent 5-foot cover.

In approximating the volume of radon emanating from overburden placed in spoil piles or replaced in pits as part of a backfilling sequence, certain assumptions were made relative to amount of uranium in the overburden and the ratio of radon to uranium. As ore grades approach the levels assumed in this study, it is expected that mine cutoff grades would be as low as .02 percent U_3O_8 with the total mine waste approaching .001 percent. Assuming an average and constant ratio of radon to uranium, the amount of radon present would be less than 1 percent of that in the tailings and should be of minimal environmental concern, despite the increased volumes of waste generated by the mining of lower-grade ores.

Control and management of tailings piles have been inadequate in the past at some uranium mills. In a study of 20 inactive mill sites, EPA (Douglas and Hans 1975) found excessive ground radiation within a half mile of tailings piles. The dispersion of the mill tailings at these sites was due largely to wind and might have been avoided by covering the piles with fill dirt and, perhaps, vegetation.

Tailings piles have also been the source of water contamination in some small areas. A study conducted in the Grants region of New Mexico (U.S. EPA 1975) showed that mill tailings have contaminated a small stream with radium-226 as well as selenium and vanadium to the extent that the water does not meet state water quality standards for irrigation or livestock watering.

The Nuclear Regulatory Commission presently views the containment of tailings as essential to any environmentally acceptable plan for milling of uranium ores. Several containment systems have been considered, all involving the lining of impoundment areas with some kind of impervious material, either compacted clay or a synthetic material (see U.S. DOE 1978a). Proposed designs for disposal systems vary somewhat but all are intended to inhibit the mobility of toxic materials left in the tailings.

Although the dispersion of radioactive substances from uranium mill tailings appears to be the environmental problem of most concern in uranium production, other types of environmental contamination need to be monitored, such as molybdenum from stack emission of plants for ashing uraniferous lignites. (G.A. Christianson and G.A. Jacobson, unpublished report of the North Dakota State Department of Health and the U.S. Environmental Protection Agency).

It seems likely that most of the problems of the past will be avoidable with strict adherence to current environmental regulations, but significant future increases in uranium production will make such adherence even more important than it is now.

PROCESSING CONSIDERATIONS

The two processing methods for U_3O_8 recovery in the United States are variations of acid leaching or alkaline leaching. From the standpoint of accessory elements, it does not make much difference which flowsheet is used. Every effort is made to recover the maximum amount of U_3O_8 consistent with the economics involved, and accessory elements such as vanadium, molybdenum, or copper are produced as byproducts only if profitable.

Because these byproduct-type elements all have significant markets and other sources of supply larger by far than the amounts associated with U_3O_8 production, their presence along with uranium is incidental and of economic importance only as it affects the revenue or cost of a particular operation.

Substantial changes in extractive metallurgical processing do not appear likely in the next 25 years, particularly changes that will affect the production of accessory elements or environmental concerns caused by them. A possible exception in this regard is the development of _in situ_ leaching processes, now being used on a limited basis in uranium mining. _In situ_ mining processes permit the mobilization and possible escape of uranium and some associated elements from the leach field and this is a principal environmental concern. Also, the fate of ammonia, introduced as a leaching reagent, is poorly known. It is possible that preventing the migration of solutions in unwanted directions will control many of the environmental problems that might otherwise develop. However, our present limited knowledge about the fate of accessory elements and compounds in the in situ leaching of uranium ores clearly points to the need for a better understanding of the redistribution mechanisms resulting from in-place mining practices.

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REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS FROM MINING AND PROCESSING OF PHOSPHATE ORES

SUMMARY

This report identifies the U.S. phosphate deposits that are most likely to be mined through the year 2000 and describes the probable redistribution of accessory elements and compounds that would result from mining and processing activities. Particular attention is given to potential adverse environmental impacts of any redistribution of elements and compounds and to the opportunities for byproduct recovery of elements associated with phosphate ores. The content and conclusions of the report are based largely on the technical literature and on the contributions of the engineers and scientists who participated in a National Academy of Sciences Workshop on Phosphate Rock Accessory Minerals, held at TVA's National Fertilizer Development Center, Muscle Shoals, Alabama, on February 24-25, 1977.

Economic phosphate deposits are found in marine sedimentary rocks, apatite-rich igneous rocks, and in modern or ancient guano deposits. However, all U.S. production comes from marine sedimentary rocks (phosphorites). The bulk of current production is from the Atlantic Coastal Plain of Florida, although North Carolina, Tennessee, Idaho, Montana, Utah, and Wyoming contribute significant amounts.

The principal phosphate ore deposits in the Atlantic Coastal Plain are essentially flat-lying beds that are covered by overburden ranging from less than 50 feet in Florida to nearly 100 feet in North Carolina. Phosphates in the western states occur in marine sedimentary deposits of great lateral extent but which are commonly found in complex structural configurations. However, most of the western ores and all the Atlantic Coastal Plain ores are mined by strip-mining methods, which involve the movement of enormous quantities of overburden and ore materials. This large-scale mining process, together with the mill processing of large tonnages of ore, can result in a significant redistribution of accessory elements and compounds. The deposits of Tennessee, in contrast to those of the Atlantic Coastal Plain and western states, are residual deposits formed by weathering of phosphatic limestones. They are small in size and irregular in shape, and thus are probably of relatively small import to the major problems of dealing with phosphate ores.

A perspective of the problems associated with mining and processing of phosphate ores may be gained from the consideration that the annual domestic production of phosphate rock may reach nearly 60 million metric tons by the year 2000. It can be expected that future mining operations will be similar to those of today in the Atlantic Coastal Plain and western states, except that deeper deposits may be worked, the scale of mining will likely increase, and grade of ore will show further decline. The potential for byproduct recovery and for impacts on the environment as a result of large-scale mining and processing of phosphate rock can be expected to increase with expanded production in the future.

Two elements, uranium and fluorine, are of particular importance both from an economic and environmental viewpoint. Marine phosphorites have an average U_3O_8 content of about .01 percent, and each year in wet-process phosphoric acid production alone uranium is present in the amount of several thousand tons. Currently, uranium is being extracted in some wet-process phosphoric acid production. It is likely that within the next decade most major producers of wet-process phosphoric acid may be recovering byproduct uranium for commercial use. The redistribution of uranium and its decay products, especially radon gas, into the environment poses a possible environmental problem that requires industry to exercise caution in waste byproduct disposal and in land reclamation operations. Additional environmental problems may result from the presence of uranium in mill slimes, in furnace dusts, and slag resulting from the thermal processing of phosphate rock.

Fluorine is present in phosphate ore concentrates in amounts between 3 and 4 percent and these ores are thus potentially a significant source of byproduct fluorine, and under favorable economic conditions could provide nearly half of the nation's needs for this element. At the same time, the handling of large quantities of fluorine compounds in processing phosphate ores creates a possible environmental hazard that is as yet not fully understood. However, the phosphate industry exercises strong controls on fluorine emissions and, although some fluorine may escape into the atmosphere through volatilization during chemical processing of ores, or into the environment via waste waters, slimes, furnace slag, precipitator dust, phosphorus sludge or other products, including fertilizers themselves, the amount lost to the environment is relatively small.

Phosphate ores also have a limited potential as a source of rare-earth elements and some minor elements. Ferrophosphorus, a byproduct of electric-furnace reduction of phosphate ores, contains vanadium and chromium, which in turn could be recovered. Similarly, the furnace precipitator dust contains small amounts of germanium and gallium available for recovery.

Future problems in the mining and processing of phosphate ores are likely to center on minimizing the use of water and developing environmentally acceptable methods of reclaiming waste lands, including wetlands.

PHOSPHATE RESERVES AND RESOURCES

Geology and Mining Methods

Economic phosphate deposits occur, in decreasing order of importance, in marine phosphorites, apatite-rich igneous rocks, and modern or ancient guano deposits. All United States production and reserves are from marine phosphorites. The origin of the phosphate within the deposits is generally hypothesized to be related to upwellings of cold phosphorus-rich oceanic waters onto shallow continental shelves or into shallow basins. A number of modes for particle formation have been suggested, including guano, manufacture by marine organisms, direct precipitation, leaching and reprecipitation, and phosphatization of limestone and marine reworking. Water depths in the depositional environment were generally less than 300 feet; most of the Atlantic Coastal Plain phosphorites were probably deposited in waters less than 100 feet deep. Some deposits are economic as a result of secondary alteration. The brown-rock phosphate deposits of Tennessee are the residuum from weathering of a phosphatic limestone in a humid climate. The Tennessee white-rock deposits and Florida "hard rock" deposits were formed by secondary phosphatic precipitation and irregular replacement of limestone. Some Florida deposits have apparently been upgraded by post-depositional ground-water leaching.

Industry practice in the United States (with the exception of Tennessee) is to express production and reserves in terms of tons of cleaned product. Chemical analyses may be reported as percent phosphorus pentoxide (P_2O_5) or as tricalcium phosphate [$Ca_3(PO_4)_2$], informally known as bone phosphate of lime (BPL). Conversion factors are: $P_2O_5 = BPL \times .4575$; $BPL = P_2O_5 \times 2.1858$; and $P = P_2O_5 \times 0.436$. The term matrix is commonly used in referring to the material of the phosphorite ore bed, or to the zone of such material and, occasionally, to the bed itself.

The residual and replacement deposits of Tennessee mostly belong to the Bigby-Cannon formation. They are relatively small in size and irregular in shape, and are stripped and mined with 2- or 3-cubic-yard draglines. Blasting to remove overburden or ore is generally not necessary. Loose clay overburden averages 8 feet in thickness but may range to 20 feet or more. The phosphate ore averages 6 feet in thickness but may be as thick as 25 feet. Most deposits are residual weathered portions of the limestone and are exposed around the rims of hillsides or in lower areas where the overlying limestones have been removed. Moving laterally into the hills, the limestone is less weathered and phosphate content is of lower grade. Ore is trucked or shipped by rail to plants where it is washed and classified to obtain a higher grade before being agglomerated to provide electric-furnace feed. Essentially all Tennessee phosphate rock is treated in electric furnaces to produce elemental phosphorus.

The principal ore bed of the Pungo River Formation (Miocene) of North Carolina is a blanket-like, relatively homogeneous, primary marine phosphorite 20 to 40 feet thick and overlain by 90 to 130 feet of sand, clay and marl overburden. Because of high potentiometric surface, the underlying aquifer must be depressurized by pumping about 60 million gallons of water per day. The matrix is approximately one-third sand-sized phosphorite pellets. After the top 35 or 40 feet of overburden is stripped off, draglines with bucket capacities as large as 72 cubic yards are used to remove the remainder of the overburden and the ore bed itself from the 40-foot bench. The matrix is slurried at the mine with high-pressure water jets and pumped to a plant where it is washed and screened to supply feed between -16 and +200 mesh for flotation cells.

Flotation concentrate is then calcined to produce a product in the 69 to 72 percent BPL range.

Existing mines in central Florida (Polk and Hillsborough Counties) are within the Bone Valley Formation (Pliocene-Miocene). In north Florida (Hamilton and Columbia Counties) the formation is of equivalent age. The overburden for both areas is less than 50 feet thick and averages about 20 feet. The deposits are characterized by predominantly quartzose and clayey matrices, 5 to 45 feet thick, in which the phosphorite pellets have been upgraded through removal of soluble impurities by weathering. The overburden of clayey sand, the leach-zone material, and the underlying matrix are selectively strip-mined by large electric-powered draglines with bucket sizes ranging from 17 to 55 cubic yards. The draglines work in cuts 150 to 350 feet wide and as much as several thousand feet long. Overburden is placed in the previously mined adjacent cut, with unavoidable mixing of the more highly uraniferous leach-zone material. The matrix is dumped into sumps dug adjacent to the mine cut on the high wall. Hydraulic guns slurry the matrix, which is then pumped through 18 to 20-inch pipe as far as 6 miles to the washing plant.

Cleaned material from the washer larger than 16 mesh in fragment size is commonly a saleable phosphate pebble-product. The fraction smaller than 16 mesh is deslimed, and feed between 16 and 150 mesh is further processed by flotation to produce a final concentrate grading 70 percent BPL or better.

Most ore within the south Florida district (in Manatee, Hardee, Sarasota, and DeSoto Counties) is assigned to the Hawthorn Formation (Miocene) similar to those of the central Florida district. However, a number of characteristics make the area inferior to the Bone Valley of central Florida. The concentrate grade will only be 65 to 68 percent BPL because of a preponderance of unweathered phosphorite pellets, and the MgO content of the rock generally will be higher, often at levels presumed deleterious to the acid-manufacturing process, due to residual rhombic carbonates, especially donomite, and a higher content of magnesium-bearing clays. The Bone Valley Formation of the central Florida mines is a dominantly quartzose clastic facies, whereas the south Florida deposits (Hardee County in particular) are in a transitional zone where a quartzose clastic facies interfingers with a dolomitic carbonate facies. Pebble phosphate, easily and cheaply recovered in central Florida, is a much smaller portion of the rock product in south Florida. And finally, the ore in south Florida is considerably lower grade than the Bone Valley. Careful geologic mapping, selective mining, and the blending of different types of matrix may be necessary to provide predictable and consistent feeds to beneficiation plants. New beneficiation procedures may also be needed to make acceptable concentrates from the more dolomitic south Florida ores.

Phosphorite deposits of the Phosphoria Formation (Permian) of the western United States are as much as 20 feet thick, have great lateral extent, and commonly occur in complex structural settings. Except for two underground mines in Montana, all phosphate ore is strip-mined. Most of the mines in southeastern Idaho use scrapers and bulldozers to remove overburden and mine the ore, much of which has been softened and upgraded by weathering. In Montana, ore broken in underground stopes is moved through loading chutes to haulage adits. In Utah, the phosphate rock is quarried after an overlying limestone cap is drilled, blasted, and removed. The ore bed is about 20 feet thick, and the total thickness of overburden and ore combined ranges from about 50 to 100 feet. Ore mined in the western states is hauled either by truck or rail to processing plants.

Western phosphate ore is commonly classified as "main bed," containing 31 to 32 percent P_2O_5 and suitable for treatment in wet-process phosphoric acid plants, and as "furnace shale," containing 24 to 26 percent P_2O_5 and commonly treated in electric furnaces. The main bed ore is usually calcined to reduce hydrocarbon impurities before further treatment. Furnace shale is nodulized to prepare a charge to the furnace that is free of fines. Furnace shale is also beneficiated by crushing, grinding, classification, filtering, and drying to produce a 31 to 32 percent P_2O_5 product for wet-phosphoric acid manufacture.

Reserves and Resources

Phosphorus is one of the earth's most common elements and the total phosphate resource is tremendous in comparison to other, rapidly depleting, mineral resources. Many rocks of the earth's crust contain phosphorus in one of several mineralogical forms and phosphate occurs commonly on most of the world's ocean floors. However, like other resources, phosphates are unevenly distributed throughout the world. Fortunately, the United States is well endowed with phosphate deposits and our identified resources measure in the billions of tons (Table 4.1). Most of these resources are in the coastal plain of southeastern United States and in the western mountain states. Our Tennessee resources are relatively small by comparison.

The proportion of our phosphate resources that can be considered "reserves" (economically recoverable resources) may increase as new deposits are discovered and as technology to treat phosphate ores is improved, but changing economic conditions may effect either an increase or decrease in reserves. It is thus difficult to provide a figure for recoverable reserves that will be meaningful for very long. Table 4.1 illustrates the impact of cost alone on designating "recoverable resources." As is shown for southeastern United States resources, a $5.00 per ton or 25 percent increase in acceptable recovery cost would more than double the "reserve" available at an extraction cost of $20.00 per ton or less. Expanding allowable cost beyond that point, of course, further increases the "reserve" and the total becomes restricted by the identification process rather than economics. The point of this comparison is to identify the problem of designating United States reserves versus world reserves. Many of the "reserves" assigned to other countries in Table 4.1 are being recovered at a cost that would be unacceptable in the United States on a free market. Only if such countries choose to compete on the world market does such a cost comparison become appropriate.

In the United States, central Florida has remained, since the early 1900s, the most important phosphate-producing area. Its exceptional deposit, which was and is being produced at a relatively low cost, will be substantially depleted by 1990 if current production levels are

TABLE 4.1 Estimated Identified World Phosphate Rock Resources--1965 and 1978 (in millions of metric tons of product)

	Product Average P_2O_5	Identified Resources Recoverable			
			As of 1978		As of 1965 6/
		Total	< $20 Product Ton	< $25 Product Ton	
NORTH AMERICA					
United States					
Florida-Central	31.5 (30-32%)	807	693	779	1,300
Florida-South 1/	30 (29-31)	1,689	667	845	
Florida-North, East	30.5 (30-32) 30.5 (30-32)	1,268	284	998	100
Subtotal Florida		3,764 1/	1,644 2/	2,622 2/	1,400
North Carolina 2/	31 (31 calcined)	1,620	413	1,509	500
Georgia, South Carolina		3,236	-	-	-
Tennessee 3/	25 (23-32)	40	36	40	75
Subtotal, Southeastern U.S.		4,896 1/	449 1/	1,549 1/	1,975
Western U.S. *	27	1,500 4/	900	900	1,200
Total U.S.		10,160	2,993	5,071	3,175
Mexico	25	1,000	-	-	-
Subtotal		11,160	2,993	5,071	3,175
SOUTH AMERICA			As of 1978		As of 1965
Brazil	20		100 6/		90
Peru-Sechura	31		500 6/		-
			600		90
WESTERN EUROPE					
France	15-20		-		-
EASTERN EUROPE					
Soviet Union - Kola	39		300 6/		360
Other	25		1,000 6/		-
			1,300		360

TABLE 4.1 (Continued)

	Product Average P_2O_5	Identified Resources: Recoverable As of 1978	Identified Resources: Recoverable As of 1965 6/
AFRICA	32	150 6/	300
Algeria	32	150 6/	300
Egypt	30	200 6/	200
Morocco	35	18,000 5/	10,000
Rhodesia	30	small	-
Senegal	37	130 5/	150
South Africa	36	3,000 5/	20
Spanish Sahara	37	400 5/	1,000+
Togo	37	50 5/	50
Tunisia	30	300 5/	600
		22,230	12,320
ASIA			
China (People's Republic)	-	-	-
Christmas Island	34	35 6/	25
India	28	10 6/	10
Israel	28	100 6/	100
Jordan	32	100 6/	65
North Vietnam	38	70 6/	100
Syria	25	100 6/	-
		415	300
OCEANIA			
Australia	30	1,000 5/	-
Nauru Island	38	50 6/	90
Ocean Island	38	5 6/	15
		1,055	105
WORLD TOTAL		36,760	16,350

1/ "Evaluation of the Phosphate Deposits of Florida Using the Minerals Availability System," Zellars-Williams, Inc. 1978.

2/ "Evaluation of the Phosphate Deposits of Georgia, North Carolina, South Carolina Using the Minerals Availability System," Zellars-Williams, Inc. 1978.

3/ "Evaluation of the Phosphate Deposits of Tennessee Using the Minerals Availability System," Zellars-Williams, Inc. 1978.

4/ Garrand, Leonard J., 1974, Phosphate Study - Southeastern Idaho: USDA, Caribou National Forest Contract No. 50-820, Unpublished.

5/ Department of Interior, United States Bureau of Mines, Mineral Commodity Summaries 1979, p. 115 (Note: U.S. Bureau of Mines amounts are in terms of "reserves.")

6/ Manderson 1977, from U.S. Bureau of Mines and British Sulfur Corp. (London).

* Resource figures cited here reflect mineral industry estimates of potential economically recoverable phosphate rock and may be lower than resource estimates presented elsewhere. (See Cathcart and Gulbrandsen [1973], Blue and Torres [1975], and Trondsen and Mead [1977].)

SOURCE: Zellars-Williams, Inc., personal communication (1979).

maintained. The depleted production is expected to be replaced principally by large reserves and resources of the south Florida area and North Carolina. Note that a $5.00 per ton increase in acceptable cost will increase the "reserves" of each of these areas by 1 billion tons.

It is important to recognize that an additional constraint in designating reserves is that of "legal extractability." Rapid population increases, competition for water, energy, and other natural resources, and the growing mining restrictions for accessibility to areas deemed "environmentally sensitive" will reduce the recovery of available resources. Offsetting any such loss to the presently identified resource is the potential for an increase through further technological innovation or deposit discovery. New discoveries are expected in the southeastern United States, principally offshore in the Atlantic and in the Gulf of Mexico. These discoveries will have to be accompanied by innovations in mining recovery not presently applied by industry. In the western states, known resources are reasonably identified; the recovery will depend on innovations in mining techniques and on costs. In addition, huge, lower-grade "hypothetical" resources exist in the phosphatic limestone underlying Florida (Hawthorn Formation), Tennessee (Bigby-Cannon and Hermitage Formations), and South Carolina (Cooper Marl Formation). These phosphorites are presently uncompetitive in extraction cost.

Production Statistics

Statistics from the U.S. Bureau of Mines indicate that United States phosphate rock production grew from 37.4 million metric tons in 1968 to 47.3 million metric tons in 1977. It is expected that by the year 2000 production will reach nearly 60 million metric tons or more. The bulk of this production (about 84 percent) now comes from the Atlantic Coastal Plain of North Carolina and Florida. About 12 percent comes from the western United States (Idaho, Montana, Utah, and Wyoming), and the remaining 4 percent comes from Tennessee. Currently available information on phosphate production is shown in Table 4.2.

Mineralogy and Accessory Elements

The chemical compositions, mineralogical forms, and structural properties of phosphorites have been extensively studied and well documented (see Lehr et al. 1968).

Sedimentary apatite has a wide range of chemical compositions. The general structural formula for marine carbonate-apatite is $Ca_{10}(PO_4, CO_3)_6Fe_{2-3}$ (Altschuler et al. 1958). Apatite is host to many substitutions by cations, anions, and anionic radicals. VO_4 and AsO_4 occur as trace substitutions for PO_4. McClellan (1977) has shown typical substitutions that can take place in fluorapatite and its carbonate-bearing varieties (see Table 4.3).

Accessory elements associated with phosphorite deposits are of two types--those associated with accessory minerals and those that are chemical substitutions within the principal phosphate mineral (usually

TABLE 4.2 World Phosphate Rock Production, 1964, 1974, and 1977 (in thousands of metric tons of product)

		Production	
	1964	1974	1977
NORTH AMERICA (incl. Central America and Caribbean)			
United States			
Florida - Central and North	17,500	31,000	
North Carolina	-	2,500	
Tennessee	2,960	2,200	
Western States	2,500	5,700	
Total United States	22,960	41,400	47,508
Other			
Mexico	27	70	70
Curacao	118	90	80
Subtotal (rounded)	23,100	41,600	47,700
SOUTH AMERICA			
Brazil	240	250	608
Venezuela	-	140	43
Columbia	-	10	10
	240	400	661
WESTERN EUROPE	60	100	149
EASTERN EUROPE			
Soviet Union	12,800	22,900	24,375
AFRICA			
Algeria	70	800	1,001
Egypt	600	600	580
Morocco	9,900	19,600	17,027
Rhodesia	-	100	140
Senegal	700	1,700	1,802
South Africa	600	1,600	2,403
Spanish Sahara	-	2,400	232
Togo	700	2,600	2,857
Tunisia	2,700	4,000	3,614
	15,270	33,400	29,656
ASIA			
China (People's Republic)	800	3,000	4,000
Christmas Island	800	1,800	1,260
India	10	400	635
Israel	240	1,000	1,232
Jordan	600	1,600	1,782
North Korea	200	400	450
North Vietnam	1,000	1,200	1,600*
Syria	-	500	425
	3,650	9,900	11,384
OCEANIA			
Australia	-	-	485
Makatea	400	-	-
Nauru Island	1,800	2,300	1,146
Ocean Island	350	600	419
	2,550	2,900	2,050
WORLD TOTAL (Rounded)	58,000	111,000	116,000

*Vietnam

SOURCE: Manderson (1977).

TABLE 4.4 Average Spectrographic Analyses of Trace Elements in High-Grade Phosphorites (in ppm)

Element	Detection Limit	Content of Av. Shale[1]	Phosphoria Fm.[2] Ida, Mont., Wyo., Utah	Bone Valley Fm.[3] Fla.	Pungo River Fm.[4] N. Ca.
Ag	0.1	0.07	.5-5	.5-5	.5-5
As	100	13	40	20	—
B	30	100	—	—	30
Ba	3	580	100	70	75
Be	0.7	3	—	1	3
Cd	10	0.3	40[5]	14[5]	20[5]
Co	1	19	—	3	—
Cr	1	90	1,000	100	175
Cu	0.3	45	100	10	60
Ga	1	19	—	—	—
Hg	—	—	10-50[7]	.01-7[7]	.085[7]
Li	30	66	—	7	7
Mn	0.7	850	30	200	10
Mo	3	2.6	30	10	7
Ni	2	68	100	15	13
Pb	1	20	—	10	20
Sb	100	1.5	7	—	—
Sc	1	13	10	7	7
Se	—	0.6	10	—	—
Sn	3	6	—	—	5
Sr	2	300	1,000	1,000	5,000
Ti	2	4,600	—	—	750
U	300	3.7	90[6]	140[6]	65[6]
V	1	130	300	150	25
Zn	100	95	300	100	200
Zr	3	160	30	50	50

[1] Turekian, K.K., and Wedepohl, K.H., 1961, Distribution of the elements in some major units of the Earth's crust, Bull., v. 72, Geol. Soc. Am., p. 175-192.

[2] Modal values of 60 analyzed samples of shaly phosphorite, Idaho, Mont., Wyo., and Utah; Gulbrandsen, R.A., 1966, "Chemical composition of phosphorites of the Phosphoria Formation:" Geo. et Cosmo. Acta, v. 30, p. 769-778.

[3] Modal values of many analyses of pellet and pebble concentrates; Cathcart, J.B., 1974, "Geology and mineralogy of phosphate rock in the Bambui Group... Minas Gerais, Brazil": U.S. Geol. Survey, Open-File Report, 59 pp.

[4] Average of pellet concentrates from 2 large-scale prospecting composites; Altschuler, Z.S., in preparation, "Chemistry of Phosphorites": Chap. X, in: U.S. Geol. Survey, Data of Geochemistry.

[5] Chemically determined. Phosphoria: av. of 6 samples, 5 localities; Bone Valley, av. of 12 samples, 7 localities; Pungo River, Av. of 2 prospecting composites; Altschuler, Z.S., *Ibid.*

[6] Chemically determined.

[7] Mercury values are provisional, as they are based on very few analyses.

SOURCE: Altschuler (1977).

TABLE 4.5 Spectrographic Analyses of Rare Earths, Yttrium, and Scandium in Primary Apatites and Secondary Phosphates (in ppm)

	Primary			Replaced or altered		
	A	B	C	D	E	F
La	150	233	1,500	0.8	0.5	400
Ce	120	140	2,700	2.0	1.2	100
Pr	30	19	500	0.11	0.07	-
Nd	70	187	1,500	1.0	0.45	5
Sm	30	18	430	<0.3	<0.3	-
Eu	4	17	20	<0.3	<0.3	-
Gd	14	16	330	0.3	0.3	5
Tb	4	4	40	0.17	<0.15	-
Dy	16	40	300	0.16	0.12	-
Ho	4	7	50	0.07	0.05	-
Er	21	44	220	0.12	0.08	-
Tm	2	2	-	<0.07	0.06	-
Yb	8	23	100	0.12	0.07	50
Lu	3	5	ND	<0.07	<0.06	-
Y	110	-	1,750	1.25	1.05	600
Sc	3	-	70*	ND	ND	2

A Average of three apatite composites, Bone Valley Fm., Florida (Altschuler et al, 1967).

B Average of three pellet concentrates, Battle Creek Fm., Australia (Cook, 1972).

C Average of 67 pyritic and organic-rich fossil fishbone fragments, Malkop and Mangyshlak deposits, USSR (Kochenov and Zinovieff, 1960).

D Carbonate-fluorapatite, supergene limestone replacement, Florida "hard-rock," Dunnellon, Florida (Altschuler, 1973).

E Hydroxylapatite, guanitized limestone, Mona Island, Puerto Rico (Altschuler, 1973).

F Lateritoid aluminum phosphate, Bone Valley Formation, Clear Springs, Florida (Altschuler, 1973).

SOURCE: Altschuler (1977).

series. This is considered further under the heading of redistribution of accessory elements.

Phosphate concentrates contain 3 to 4 percent fluorine. Nash and Blake (1977) estimate that, if the fluorine contained in phosphate ores currently being processed for fertilizers in this county were recovered, nearly half of the Nation's needs for fluorine could be met. In fact, some of the fluorine volatilized during processing is now being recovered. Fluosilicic acid is the principal fluorine compound recovered, and it finds markets in water fluoridation and aluminum manufacture. It is probable that the fluorine recovery from phosphate fertilizer plants will expand in the next decade.

DISTRIBUTION OF NONPHOSPHORUS CONSTITUENTS IN MINING AND BENEFICIATION

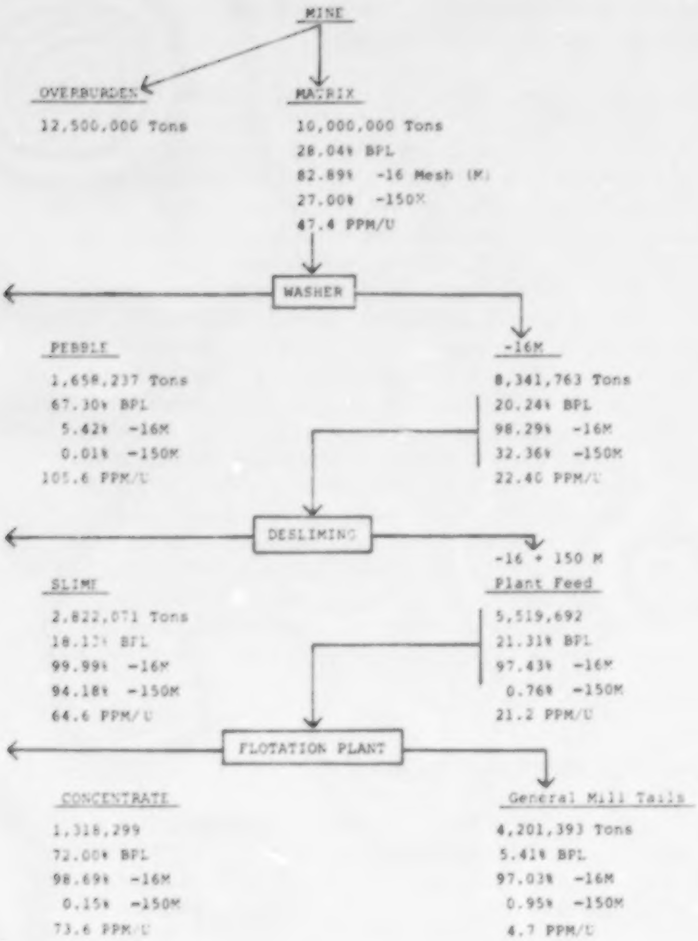
Commercial phosphate rock concentrates contain a large number of nonphosphorus constituents (see Tables 4.3 and 4.4). Many of these accessory constituents occur in solid solution in the apatite structure and can only be extracted by chemical methods. Their distribution during raw-material processing simply follows the distribution of the apatite itself. If the mining and concentration processes could be carried out at 100 percent recovery, all of the nonphosphorus constituents associated with the apatite or carbonate-apatite grains would be extracted from the ground and contained in the mineral concentrate. Actually, the overall recovery of P_2O_5 in product concentrates is rarely greater than about 75 percent of the values contained in the matrix. Mining techniques result in ore (matrix) recoveries of 85 to 90 percent. Milling practices create a further loss of P_2O_5 in waste reject. For example, in central Florida essentially all of the pebble phosphate larger than +16 mesh and about 70 to 90 percent of the P_2O_5 values in the -16 to +150 mesh plant feed are recovered, but about 20 percent of the P_2O_5 values in the matrix are lost in slimes in cases of high-grade, fine-grained ore. The losses of P_2O_5 to the slimes vary widely from ore body to ore body depending on the size and P_2O_5 distribution of the phosphate particles in the matrix. In south Florida, slime losses are usually somewhat lower than in the Central District.

Typical Material Flows

The flowsheet in Figure 4.1 shows the distribution of phosphorus (BPL-grade) and uranium (parts per million) for a typical central Florida operation. This operation is designed to move about 12.5 million tons of overburden in order to mine 10 million tons of matrix, producing about 3 million tons of product (pebble and concentrate), 3 million tons of slimes, and about 4 million tons of tailings.

The uranium concentration in phosphate deposits differs considerably. As previously mentioned, it can be assumed that the uranium daughters through radium-226 (^{238}U --> ^{234}Th --> ^{234}Pa--> ^{234}U --> ^{230}Th --> ^{226}Ra) are in secular equilibrium. Thus a radiometric analysis of radium-226, for example, allows calculation of any of the isotopes in secular equilibrium. On the flowsheet in Figure 4.1, the uranium concentration in the pebble-product is 105 parts per million and in the concentrate about 74 parts per million. Averages for the Florida districts are somewhat higher--about 140 parts per million for pebble material and 100 parts per million in concentrates. About 60 percent of the uranium values in the matrix are recovered in the pebble and concentrate products. Most of the uranium losses occur in the slimes.

Uranium concentrations in south Florida in the combined pebble and concentrate product are somewhat lower than in the Central District. A lower percentage of pebble in the matrix is common and this is partly responsible for the lower uranium average. However, in general, the uranium content appears to be lower in all the phosphate grains.


MINE
OVERBURDEN
12,500,000 Tons
MATRIX
10,000,000 Tons
28.04% BPL
82.89% -16 Mesh (M)
27.00% -150M
47.4 PPM/U
WASHER
PEBBLE
1,658,237 Tons
67.30% BPL
5.42% -16M
0.01% -150M
105.6 PPM/U
-16M
8,341,763 Tons
20.24% BPL
98.29% -16M
32.36% -150M
22.40 PPM/U
DESLIMING
SLIME
2,822,071 Tons
18.13% BPL
99.99% -16M
94.18% -150M
64.6 PPM/U
-16 + 150 M
Plant Feed
5,519,692
21.31% BPL
97.43% -16M
0.76% -150M
21.2 PPM/U
FLOTATION PLANT
CONCENTRATE
1,318,299
72.00% BPL
98.69% -16M
0.15% -150M
73.6 PPM/U
General Mill Tails
4,201,393 Tons
5.41% BPL
97.03% -16M
0.95% -150M
4.7 PPM/U

SOURCE: Lawver (1977).

FIGURE 4.1 Typical flow sheet for a central Florida operation.

Accessory Elements in Slimes

Figure 4.1 shows that less than one-third of the matrix is rejected as slimes. Tables 4.6, 4.7, and 4.8 show the mineralogical and chemical composition and the size distribution of typical central Florida slimes. The actual percent of the matrix rejected as slimes and the slime material composition varies widely within the individual ore bodies and across the field.

Water Requirements, Water Discharge, and Water Quality

In Florida phosphate production, water is used for the ore transportation and beneficiation. Water is required in attritioning the matrix, as a medium for transporting the matrix, and in separating the pebble, sand and clay-size fractions at the washer. Water acts as a

TABLE 4.6 Chemical Analyses of Slime Solids (Central Florida)

Constituent	Typical, Percent	Range, Percent
P_2O_5	9.06	9 - 17
SiO_2	45.68	31 - 46
Fe_2O_3	3.98	3 - 7
Al_2O_3	8.51	6 - 18
CaO	13.95	14 - 23
MgO	1.13	1 - 2
CO_2	0.8	Trace - 1
F	0.87	Trace - 1
Loss on ignition at 1,000°	10.6	9 - 16
BPL	19.88	19 - 37

SOURCE: Lawver (1977).

medium in size classification and in flotation processes. It is also used as a method for transporting sand tailings and slimes from the plant to disposal and reclamation areas. The recovery of water from waste, together with recirculation of water in the system, is essential since the volume required for the operation is very large and exceeds the amount of new water coming into the system. The mine systems are generally designed to recirculate in excess of 90 percent of the water required to conduct all the various beneficiation and washing steps.

Losses of water from the circuit occur mainly due to entrainment of water in the sand tailings and adsorption of water in the clay waste fractions. Other losses such as evaporation and seepage from impoundment areas are also significant. Losses occur due to shipment of wet rock or drying of wet rock. In periods of rainfall which exceed the safe containment capacity, water may be discharged and lost from the

TABLE 4.7 Size Distribution of Minus 150-mesh Slimes (Central Florida)

	Weight Percent	
	+20 μm	-20 μm
Plant A Sample #1	2.8	97.2
Plant A Sample #2	1.2	98.8
Plant B Sample #1	5.9	94.1
Plant B Sample #2	5.8	94.2

SOURCE: Lawver (1977).

TABLE 4.8 Mineralogy of Minus-150 Mesh Slimes (Central Florida)

	>50%	30-50%	15-30%	<15%
Plant A Sample #1		apatite smectite	dolomite palygorskite	quartz
Plant A Sample #2		apatite smectite	palygorskite	quartz kaolin crandallite dolomite illite
Plant B Sample #1	smectite			quartz, feldspar apatite, wavellite dolomite, illite kaolin
Plant B Sample #2	smectite			quartz, dolomite apatite, crandallite feldspar, wavellite illite

SOURCE: Lawver (1977).

system. These losses are balanced by water primarily from matrix moisture, deep well pumping, and in minor amounts from shallow wells. Surface water from local streams may also serve as makeup water. Rainfall into the various portions of the operating system is also a source of water, if it is collected and retained in the system.

The makeup water requirement is a direct function of the losses which are incurred. Generally, each mine has a similar type system but the total water requirements can vary widely due to the production rate, the composition of the ore, the dewatering characteristics of the clay, and the methods of water management and reclamation techniques. The amount of water in the system will, of course, change in response to shifts in rainfall, evaporation, seepage, and surface runoff into the system. Most of these effects are seasonal. However, it is the nonseasonal changes that are the more significant. Each system should be evaluated based on its unique requirements and considering the major variables of matrix characteristics (the most important being product-to-slime ratio), system design, and losses, plus many other variables.

The evaporation rate in central Florida is approximately 57 inches per year whereas rainfall is in the range of 50 to 54 inches per year. Some accumulation of rainfall, of course, occurs in the mining system and this can offset the losses by evaporation. However, by proper design and installation of water storage facilities in clay-settling areas and other containment areas the total water acquired by rainfall exceeds the losses by evaporation.

Slimes from most typical central Florida operations will settle to only about 18 percent solids even if allowed to stand over long periods of time. This results in each ton of slimes tying up about 4.5 tons of water. Tailings and concentrate will retain as interstitial water about .2 ton of water per ton of solids. Thus, for the case as outlined in Figure 4.1 the total system will retain approximately 5 tons of water per ton of product produced. The water consumption of 5 tons per ton of final product is typical for many central Florida operations. However, it is not a rule since some operations contain significantly less clay and consequently tie up considerably less water. The actual amount of water required for each ore body must be determined before estimating water usage.

There are a number of methods for mitigation of water loss in the mining and waste disposal process. One of the most important is water conservation. Through proper water management, water discharge can be minimized.

It is the practice in some locations to allow water to be injected into the Floridian aquifier by the use of recharge wells. This practice consists of drilling connector wells between the surficial and the Floridian aquifier and allowing water from the surficial aquifier to drain into the deep aquifier when the potentiometric surface in the lower aquifier allows sufficient head for the drainage to occur. This type of water recharge plays an important role in balancing the use of water in the mine with the amount of water withdrawn from the deep aquifier.

Improved methods of waste disposal such as sand/clay mix techniques, which are designed to improve land reclamation by increasing the stability of the waste clay, also result in additional release of water from the clays. For example, under proper conditions of sand to clay mixing and depositing of the clays, wastes can be consolidated to as much as 30 to 40 percent solids. This results in release of additional water which may be recycled to the plant. It is not practical to design all systems for total impoundment (zero discharge) due primarily to the unusually seasonal nature of rainfall in Florida. The rain comes primarily in the summer months and may fall in relatively short periods of time. In this latter event there is a rapid buildup of rainwater, necessitating the discharge of water from the processing and storage system. The water discharged to streams from processing plants compares favorably in most accessory constituents with that from a deep well (Table 4.9).

Disposal of slimes is still a major problem in existing operations and will probably continue to present a problem in the future. The phosphate content of slimes in present typical central Florida operations is about 12 percent P_2O_5 (26 percent BPL), and represents a 20 percent loss in BPL recovery from the matrix. The P_2O_5 content of slimes from future mining operations in the Southern District will range from 2 to 6 percent BPL and average only about 5 percent. This is a significantly lower loss of P_2O_5 since the Southern District average grain size of phosphate is larger and the ore is leaner than in other districts.

The Florida phosphate industry has been engaged for a very long period (since the early 1960s) in an extensive program of research and development for methods of slimes disposal. Since 1972 a cooperative research program has been under way, including members of the phosphate industry and the U.S. Bureau of Mines. Three approaches to improve slimes disposal have been developed:

1. A sand/slime technique whereby sand is sprayed into a thickened clay slime.
2. A flocculation process in which sand and clay slimes are mixed in a mechanical thickener.

TABLE 4.9 Comparison of Quality of Deep-Well Water with Discharge Water

	Deep Well	Discharge	
		Avg.	Max.
T. Sol. (ppm)	319	243	268
T. Dis. Sol. (ppm)	310	213	242
T. Sus. Sol. (ppm)		10.4	
T. Vol. Sol. (ppm)	13		25
NH_3 (N) (ppm)	.23	.28	.75
KjN (N) (ppm)	1.00	1.03	1.60
NO_3 (n) (ppm)	.20	1.60	3.20
Tot. P (ppm)	.28	.65	1.68
Hardness (ppm)	165	183	216
Br (ppm)	5.70	5.20	9.90
Cl (ppm)	8	11	12
F (ppm)	.45	1.70	2.15
NO_2 (N) (ppm)	<.02	<.01	<.02
SO_4 (S) (ppm)	20.9	18.2	37.7
S (ppm)	4.5	1.3	2.7
Al (ppm)	.094	.165	.270
Co (ppm)	<.01	.015	.018
Cr (ppm)	<.01	.008	.013
Cu (ppm)	<.01	.009	.013
Fe (ppm)	.052	.060	.220
Pb (ppm)	.060	.039	.045
Mn (ppm)	.010	.015	.020
Hg (ppb)	<.05 ppb	<.05 ppb	<.05 ppb
Ni (ppm)	.050	.044	.050
Zn (ppm)	.010	.038	.050
Oil & Grease (ppm)	1.4	2.5	5.1
Mg (ppm)	17	18	24
K (ppm)	.88	.77	.98
Na (ppm)	7	14	17
Cd (ppm)	.01	.01	.01
Gross Alpha Radiation	1.7	4.1	7.0

SOURCE: Lawver (1977).

3. A process in which dewatered tailings are mixed with prethickened clay, which has been dredged from conventional settling ponds.

Mines planned in the near future will probably incorporate one or more of the above methods of waste disposal. One of the main reasons that this will be practical is that the newer mines have leaner ore where the sand to clay ratio is more favorable for these types of disposal. As mentioned previously, this will result in more water being released from the slimes and will probably significantly reduce the water consumption per ton of product produced, maybe as much as 50 percent.

Redistribution of Uranium

The redistribution of uranium, and its radioactive decay products, as a result of mining and processing phosphate rock, can be extensive. Of particular note is the relatively high content of uranium in the leached zone, or aluminum phosphate zone, just above the matrix (Table 4.10).

The basal enriched part of the leached zone is commonly 1 to 3 feet thick, and in many areas its uranium content is known to range from 100 to 300 parts per million (Altschuler et al. 1958). On the average, the phosphatic part of the leached zone has about twice the uranium concentration of its counterpart in the underlying matrix. However, in areas of future mining, south of those currently being worked in central Florida, the leached zone is less well developed and generally is less uraniferous. Leached-zone material is of concern because it is discarded in mining as part of the overburden, thus providing a possible redistribution pathway for radon-222 into the atmosphere or into buildings in subsequently reclaimed areas, unless precautions are taken to avoid this.

In beneficiation, some uranium is lost to the slimes. However, the amount of radioactive material in slimes differs from one area to another because it is related to BPL content, or to the content of calcium aluminum phosphates, which varies from area to area. Thus, sand/clay mixes resulting from the treating of slimes from south Florida will probably be considerably less radioactive, on the average, than those of central Florida.

Accessory Elements in Concentrates

The phosphate industry routinely analyzes pebble and flotation concentrates for the elements shown in Tables 4.11 and 4.12. Tables 4.13 and Table 4.14 show typical chemical analyses of spiral and flotation concentrates from several Florida beneficiation plants. Table 4.15 gives similarly typical analyses for pebble concentrates.

Heavy Minerals

Florida phosphate deposits contain small amounts of heavy minerals, principally rutile, zircon, ilmenite, and traces of monazite. The

TABLE 4.10 Commonly Encountered Ranges of Uranium in Currently Mined Areas of Central Florida

	Areas of Unaltered Rocks	Areas of Altered Rocks		
Overburden	Upper sands	Upper sands	1-5 ppm U	Overburden
	Clayey sands	Clayey sands	1-20 ppm U	
	Matrix 50-100 ppm U	Upper leached zone	10-100 ppm U	
		Lower leached zone	50-300 ppm U	
		Matrix	50-100 ppm U	

SOURCE: Adapted from Altschuler et al. (1958).

TABLE 4.11 Comparison of Florida Phosphate Rock
100% Analysis - Approximate Shipping Grades
72% BPL - Run-of-mine Concentrates

Dry Basis	Plant One	Plant Two	Plant Three	Plant Four	Plant Five	Plant Six
$Ca_3(PO_4)_2$	72.37	72.21	72.61	72.25	72.48	72.17
P_2O_5	33.12	33.05	33.23	33.15	33.17	33.03
CaO	48.22	47.29	47.20	47.47	47.56	48.00
Fe_2O_3	1.53	0.98	1.00	1.36	1.46	1.01
Al_2O_3	1.31	1.45	1.52	1.18	0.76	1.14
CO_2	2.98	2.65	2.78	3.11	3.38	3.40
SO_3	0.51	0.69	0.55	0.75	—	—
SiO_2	7.69	8.24	8.76	7.62	6.84	—
K_2O	0.10	0.05	0.76	—	—	—
Na_2O	0.25	0.09		—	—	—
MgO	0.35	0.46	0.44	—	—	0.35
MnO	0.036	0.11	0.04	—	—	—
TiO_2	0.081	—	0.05	—	—	—
As_2O_3	0.0016	—	—	—	—	—
Cr_2O_3	0.009	—	—	—	—	—
F	3.70	3.70	3.70	3.84	3.96	3.77
Cl	0.015	—	—	0.18	—	—
	0.46	2.12		—	—	—
H_2O	1.93		1.30	—	—	
	4.28	—	—	—	—	5.68
CaO/P_2O_5	3.68	3.62	3.59	3.62	3.63	3.68

SOURCE: Lawver (1977).

TABLE 4.12 Comparison of Florida Phosphate Rock
100% Analysis - Approximate Shipping Grades
68% BPL - Run-of-mine Pebble

Dry Basis	Plant One	Plant Two	Plant Three	Plant Four	Plant Five	Plant Six	Plant Seven
$Ca_3(PO_4)_2$	68.30	69.13	68.76	69.18	68.67	68.48	68.17
P_2O_5	31.26	31.64	31.47	31.66	31.43	31.34	31.15
CaO	45.96	45.91	45.96	45.04	45.07	47.32	47.52
Fe_2O_3	1.48	0.66	1.44	1.93	1.97	1.01	1.60
Al_2O_3	1.38	2.04	1.23	1.82	1.16	1.21	0.84
CO_2	3.67	3.59	3.92	3.20	3.72	5.04	3.04
SO_3	0.82	1.00	1.04	0.69	—	—	1.30
SiO_2	9.55	9.45	9.01	9.84	9.24	—	—
K_2O	0.15	0.06	0.90	—	—	—	0.19
Na_2O	0.22	0.10		—	—	—	0.54
MgO	0.37	0.31	0.40	—	—	1.15	0.50
MnO	0.02	0.06	0.02	—	—	—	0.02
TiO_2	0.09	—	0.05	—	—	—	0.04
As_2O_3	0.012	—	—	—	—	—	0.00
Cr_2O_3	0.017	—	—	—	—	—	Trace
F	3.70	3.75	3.57	3.68	3.79	3.36	3.50
Cl	0.012	—	—	0.27	—	—	—
	0.60	2.57		—	—	—	2.09
H_2O	2.17		2.40	—	—	—	
	8.81	—	—	—	—	7.35	7.68
CaO/P_2O_5	3.72	3.67	3.69	3.60	3.63	3.82	3.86

SOURCE: Lawver (1977).

TABLE 4.13 Typical Analysis of Concentrates from Selected Central Florida Beneficiation Plants (in percent, and parts per million where indicated)

	Spiral Concentrate		Final Concentrate		
	Plant 1	Plant 2	Plant 2	Plant 1	Plant 3
Percent					
BPL	68.41	69.36	72.39	72.84	75.85
P_2O_5	31.31	31.74	33.12	33.33	34.71
Fe_2O_3	.97	1.50	1.90	1.12	.70
Al_2O_3	1.05	1.07	.87	1.06	1.18
I&A*	2.02	8.57	2.77	2.18	1.88
Insoluble	9.01	7.20	4.02	3.36	3.54
CaO	45.22	46.93	48.23	48.02	49.86
MgO	.40	.35	.36	.38	.22
K_2O	.118	.075	.073	.116	.040
Na_2O	.50	.61	.59	.60	.48
CO_2	3.29	3.95	3.91	3.64	3.81
SO_3	.37	.38	.37	.49	.30
Total S	.39	.36	.35	.48	.28
SiO_2	10.33	7.80	3.83	4.01	3.70
F	3.58	3.75	3.70	3.83	3.80
Cl	—	.0039	.029	—	.006
Organic Material	.88	.75	.53	.72	.460
LOI**	6.29	6.79	7.10	6.81	5.81
ppm					
As	7.2	6.1	8.1	9.7	5.4
Cd	4.0	5.8	6.9	4.9	18.7
Cu	8.9	11.1	12.4	9.3	17.2
Mo	13.4	11.2	12.7	13.6	7.8
Ni	28.6	24.9	36.7	30.3	30.7
Zn	39.9	57.2	68.5	52.2	135.9

SOURCE: Lawver (1977).

matrix contains from .1 to .2 percent heavy minerals with specific gravity greater than 2.95. These minerals are collected both by a fatty acid phosphate float and by the amine circuitry float. About half of the heavy minerals in the deslimed matrix go into the amine tailings and the other half into the final flotation concentrate. Figures 4.2 and 4.3 show the approximate heavy mineral distribution of a typical Florida beneficiation flowsheet, starting with the amine section feed. Heavy minerals could be recovered easily if the economics were favorable.

DISTRIBUTION OF NONPHOSPHORUS CONSTITUENTS IN CHEMICAL PROCESSING

Before it can be used, the P_2O_5 in phosphate rock must be freed from the crystalline structure of the apatite. Table 4.16 (Shreve 1967) shows the principal processes used to accomplish this, their products, and important byproducts.

In the United States, about 88 percent of the P_2O_5 value in phosphate rock is used in producing fertilizers (Stowasser 1979). The remaining phosphate rock goes primarily into the production of high-grade furnace-quality phosphoric acid and elemental phosphorus. The furnace acid in turn is used for a variety of purposes, but mainly in

TABLE 4.14 Analyses of Concentrate from Hardee County, Florida (in percent or parts per million)

Sample No.	#1			#2			#3			#4		
Conc. Size	-28	+28	Pebble	-28	+28	Pebble	-28	+28	Pebble	-28	+28	Pebble
BPL	67.79	65.89	65.32	68.16	65.05	62.34	62.91	58.14	59.22	63.45	58.24	61.58
P_2O_5	31.02	30.15	29.89	31.19	29.77	28.53	28.79	26.61	27.10	29.04	26.65	28.18
CaO	47.32	45.52	45.52	47.52	45.52	44.34	46.52	44.13	43.34	46.72	43.93	45.03
Fe_2O_3	1.71	1.40	1.55	1.91	1.79	1.74	1.54	1.52	1.47	1.60	1.56	1.54
Al_2O_3	0.82	1.00	1.20	0.83	0.77	0.87	0.67	0.68	0.84	0.72	0.69	0.77
F	3.43	3.15	3.20	3.42	3.32	3.30	2.80	2.88	2.90	3.25	2.92	3.25
MgO	.75	.72	.92	.85	.90	1.24	1.72	2.06	1.75	1.58	2.09	1.44
Na_2O	.79	.84	.74	.80	.75	.75	.82	.83	.79	.84	.81	.84
K_2O	.19	.17	.15	.19	.19	.18	.19	.16	.19	.19	.18	.18
SO_3	.59	.54	.51	.55	.55	.55	.54	.60	.60	.61	.62	.61
SiO_2	3.92	6.86	7.10	4.17	6.62	8.19	4.64	8.14	8.97	4.46	7.40	6.27
Cl	—	—	—	—	—	—	—	—	—	—	—	—
CO_2	4.20	4.30	4.66	4.50	4.50	6.24	6.39	7.06	5.83	6.09	7.16	6.24
Organic C	.61	.60	.61	.59	.60	.72	.59	.60	.80	.61	.69	.56
Sulf. S.	.51	.46	.51	.50	—	.50	.48	.49	.54	.53	.57	.33
H_2O	1.48	1.18	1.42	1.10	1.18	1.40	1.34	1.22	1.54	1.20	1.30	1.62
Insol	2.13	4.99	5.53	2.33	4.60	6.50	2.89	6.77	7.10	2.73	5.99	4.67
*LOI @1,000°C.	8.26	8.12	8.28	7.99	8.67	10.57	10.29	10.60	10.12	9.66	10.71	10.62
U_3O_8	0.009	0.010	0.011	0.009	0.010	0.012	0.009	0.011	0.012	0.009	0.010	0.012
As (ppm)	1.2	18.00	28.9	.5	34.	27.0	.2	21.6	30.6	11.4	42.	Ins. Sample
Cd (ppm)	5.6	3.9		4.7	4.2		5.2	4.6		5.2	4.5	
Pb (ppm)	17.2	10.2		14.2	11.3		14.0	6.9		15.0	10.3	
Hg (ppb)	72.9	48.7		50.0	36.7		57.4	36.5		44.6	40.0	

* Loss on ignition

SOURCE: Lawver (1977).

TABLE 4.15 Typical Analysis of Pebble Concentrates from Selected Central Florida Beneficiation Plants (in percent, and parts per million where indicated)

	Plant 1	Plant 2	Plant 3	Plant 4	Plant 5
Percent					
BPL	66.40	66.90	66.89	67.77	68.85
P_2O_5	30.39	30.62	30.61	31.01	31.51
Fe_2O_3	1.12	1.75	2.35	1.05	.85
Al_2O_3	1.07	1.07	.96	1.21	1.19
I&A*	2.19	2.82	3.31	2.26	2.04
Insoluble	7.76	9.96	7.51	9.30	10.93
CaO	46.27	45.41	46.14	46.16	45.92
MgO	.86	.35	.42	.34	.37
K_2O	.107	.071	.075	.120	.037
Na_2O	.63	.61	.666	.53	.495
CO_2	4.63	3.91	4.37	3.41	3.73
SO_3	.45	.39	.42	.40	.34
Total S	.47	.37	.39	.40	.30
SiO_2	8.81	10.20	8.28	11.70	10.39
F	3.56	3.68	3.65	3.60	3.57
Cl	—	.007	.004	—	.005
Organic Material	.67	.50	.52	.68	.412
LOI**	7.19	6.23	7.22	6.00	6.03
Ppm					
As	6.1	4.6	7.3	7.6	2.6
Cd	3.5	4.9	4.5	3.9	15.9
Cu	8.5	10.9	10.4	8.7	16.4
Mo	12.9	13.0	19.7	20.9	3.6
Ni	24.9	25.7	28.8	24.8	29.5
Zn	38.6	41.7	57.3	33.7	105.8

SOURCE: Lawver (1977).

the production of sodium tripolyphosphate for detergents, and dicalcium phosphate for animal-feed supplement. Worldwide, about 90 percent of the P_2O_5 is used for fertilizer (Manderson 1977).

Distribution in Acidulation Processes

Parks (1977) and Zellars and Williams (in press) have provided much of the following simplified description of the acidulation processes and tables showing the percentages of components of the raw rock that appear in the products of the various acidulation processes.

Wet-Process Phosphoric Acid by the Conventional Dihydrate Process

In this process, finely ground phosphate rock, water, recycled phosphoric acid slurry, and sulfuric acid are brought together in a vessel lined with carbon brick and rubber in which the phosphate and other components of the ore are agitated, dissolved, and then partly precipitated. The undissolved components and the newly formed insoluble compounds are separated from the phosphoric acid liquid phase by filtration. The liquid phase (about 40 percent H_3PO_4 or 30 percent

P_2O_5) is retained, and the filter cake is discharged to a waste storage area. The liquid phase may be used directly, or concentrated in vacuum evaporators to 54 percent P_2O_5 (approximate 100 percent H_3PO_4), or concentrated further in super acid evaporators to as high as 72 percent P_2O_5. The grade of the rock used in wet-process phosphoric acid plants commonly ranges from 64 to 68 percent BPL.

Amine Feed

525 T/hr.
0.71% Heavy Minerals (HM)

HM Composition	%	T/Hr.
Zircon	22	0.8
Rutile	5	0.2
Opaque Minerals	31	1.2
Other Minerals	42	1.6
Total	100	3.8

Amine Tail

75 T/Hr.
2.69% Heavy Minerals

HM Composition	%	T/Hr.	Distribution*
Zircon	21	0.4	61
Rutile	7	0.1	65
Opaque Minerals	28	0.6	40
Others	44	0.9	56
Total	100	2.0	50

Final Concentrate

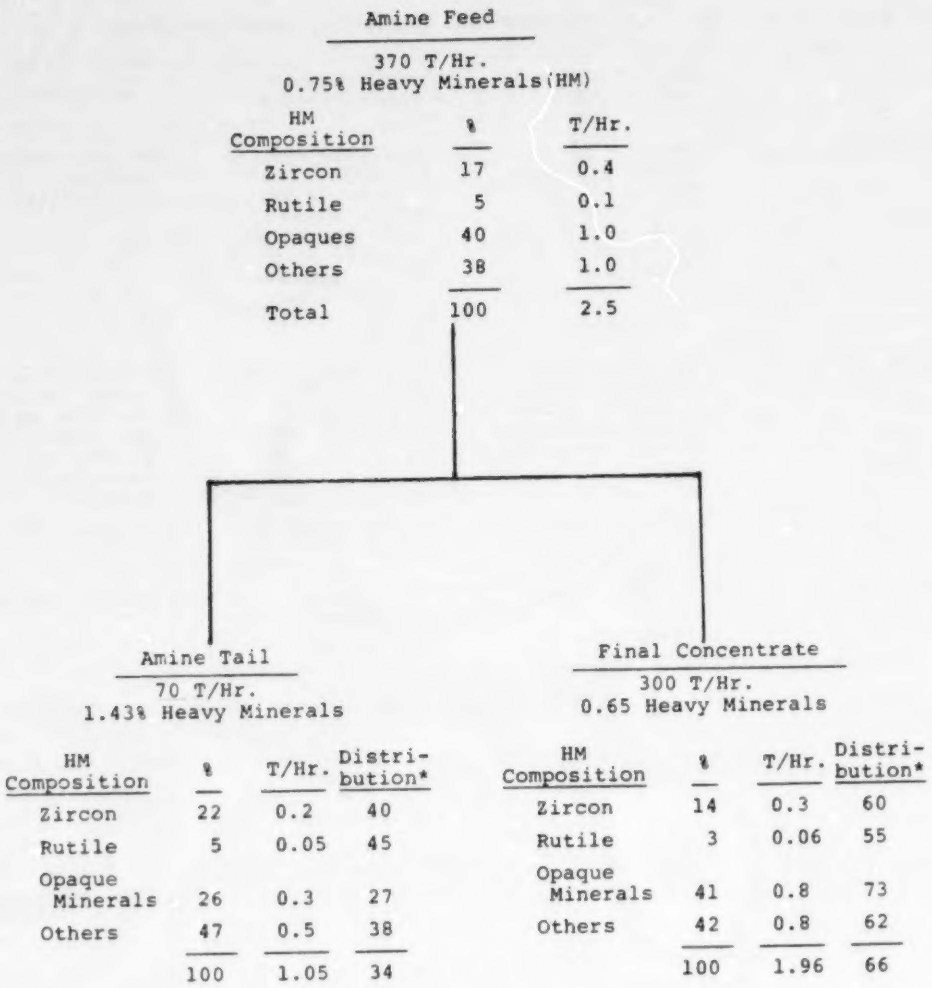
450 T/Hr.
0.49% Heavy Minerals

HM Composition	%	T/Hr.	Distribution*
Zircon	14	0.3	39
Rutile	4	0.1	35
Opaque Minerals	43	0.9	60
Others	39	0.8	44
Total	100	2.1	50

*In percent recovery

SOURCE: Lawver (1977).

FIGURE 4.2 Heavy mineral distribution in an amine circuit–525 tons per hour.



Amine Feed

370 T/Hr.
0.75% Heavy Minerals (HM)

HM Composition	%	T/Hr.
Zircon	17	0.4
Rutile	5	0.1
Opaques	40	1.0
Others	38	1.0
Total	100	2.5

Amine Tail

70 T/Hr.
1.43% Heavy Minerals

HM Composition	%	T/Hr.	Distribution*
Zircon	22	0.2	40
Rutile	5	0.05	45
Opaque Minerals	26	0.3	27
Others	47	0.5	38
	100	1.05	34

Final Concentrate

300 T/Hr.
0.65 Heavy Minerals

HM Composition	%	T/Hr.	Distribution*
Zircon	14	0.3	60
Rutile	3	0.06	55
Opaque Minerals	41	0.8	73
Others	42	0.8	62
	100	1.96	66

*In percent recovery

SOURCE: Lawver (1977).

FIGURE 4.3 Heavy mineral distribution in an amine circuit—370 tons per hour.

Nitric Phosphates

In this process, phosphate rock, often unground, is mixed with 40 to 60 percent excess HNO_3 in stainless steel vessels to produce a solution that may be filtered or decanted to remove insoluble matter (mainly quartz) before being processed into fertilizer materials. In one process (the Odda process) the acidulated mass is chilled to precipitate calcium nitrate tetrahydrate; in another, sulfuric or phosphoric acid is mixed with the acidulate. In both, the acidic mixture is neutralized with ammonia to produce a solid nitrogen and phosphorus fertilizer. The

TABLE 4.16 Phosphate-Rock Processing, Products, and Byproducts

Process	Raw materials and reagents	Main products and derivatives	By-products
Acidulation	Phosphate rock, sulfuric acid, nitric acid, phosphoric acid, ammonia, potassium chloride	Superphosphate, phosphoric acid (wet process), triple superphosphate, monoammonium phosphate, diammonium phosphate, monopotassium phosphate	Fluorine compounds, vanadium, uranium (limited)
Electric furnace reduction	Phosphate rock, siliceous flux, coke (for reduction), electrical energy, condensing water	Phosphorus, phosphoric acid, triple superphosphate, various Na, K, NH_4, Ca salts; phosphorus pentoxide and halides	Fluorine compounds, carbon monoxide, slag (for RR ballast, aggregate fillers, etc.) ferrophosphorus, vanadium*
Calcium metaphosphate	Phosphate rock, phosphorus, air or oxygen fuel	Calcium metaphosphate	Fluorine compounds
Calcination or defluorination	Phosphate rock silica, water or steam, fuel	Defluorinated phosphate	Fluorine compounds

*Vanadium is present only in appreciable quantities only in the western phosphates.

SOURCE: From Chemical Process Industries, Third Edition by R.N. Shreve. Copyright (c) 1967. Used with permission of McGraw-Hill Book Company.

calcium nitrate is also used as a fertilizer called CAN. The grade of the rock used in nitric phosphate plants is generally above 70 percent BPL.

Superphosphates

Finely ground phosphate rock is mixed, in this process, with: (a) sulfuric acid, to produce normal superphosphate; (b) phosphoric acid, to produce triple superphosphate; or (c) sulfuric-phosphoric acid mixtures, to produce double superphosphate.

The grade of ground rock used in this procedure may be as low as 68 percent BPL (31 percent P_2O_5), but ordinarily it is 72 percent BPL or higher.

Element Redistribution by Process TYpe

Tables 4.17, 4.18, and 4.19 show the wide range of nonphosphorus elements and their concentration ranges in phosphate rock products used for chemical processing. All of the solubilized nonphosphorus elements, except some volatilized fluorine, report mainly to the acid intermediate (liquid phase) and ultimately to the fertilizer products; some are removed by precipitation in byproduct cake. The amount of fluorine released as a gas or retained in byproducts is a function of the process and varies widely depending on the system employed to upgrade the phosphate rock. The amount of fluorine retained in the 54 percent P_2O_5 merchant-grade acid produced by the dihydrate process will usually be in the range of 10 to 20 percent of the fluorine in the rock. The nitric acid phosphate may contain as much as 40 to 90 percent of fluorine originally in the rock. In the dihydrate process, fluorine is evolved during the acidulation step as a gas, silicon tetrafluoride. Fluorine is retained in the gypsum cake as simple or complex fluoride salts or as a fluosilicate and is sent to waste storage ponds where it may become partially remobilized as a volatile gas (HF or SiF_4) due to solid-phase alterations in contact with pond liquor. The evaporation of the 30 percent P_2O_5 acid up to 54 percent P_2O_5 results in a large release of silicon tetrafluoride. Usually, 35 to 45 percent of the total fluorine in the rock is released in this step. In most processes this is where the fluorine is recovered as fluosilicic acid.

Other processes, such as those used in the production of triple superphosphate, single superphosphate or double superphosphate, release fluorine as silicon tetrafluoride during the acidulation process. Scrubbers are employed in these processes to remove the silicon tetrafluoride and recover it as a fluosilicic acid.

TABLE 4.17 Assay Ranges for Central Florida Phosphate Ores

Oxide	Weight Percent	Element	Weight Percent
P_2O_5	28-35	P	12.2-15.3
BPL, nominal	62-77		
CaO	44-50	Ca	31.4-35.7
MgO	0.2-1.0	Mg	0.12-0.60
Fe_2O_3	0.5-2.4	Fe	0.35-1.68
Al_2O_3	0.3-1.5	Al	0.16-0.80
Na_2O	0.3-0.8	Na	0.22-0.59
K_2O	0.06-0.24	K	0.05-0.20
		F	3.3-4.0
	parts per million		
		Zn	10-100
		Se	0.7-7.0
		Pb	10-50
		Cd	4-30
	pico curies/gram		
		U-234	40-45
		U-235	40-45
		Ra-226	38-48

SOURCE: Lawver (1977).

TABLE 4.18 Percent of Rock Components in Phosphoric Acid Made by the Dihydrate Process

	30% P_2O_5 Filter Acid	54% P_2O_5 Merchant Acid
Fe_2O_3	85-100	55-100
Al_2O_3	70-100	65-100
CaO	Less than 1	Less than 0.1
MgO	90-100	80-90
Na_2O	20-30	5-10
K_2O	50-60	1-10
Zn	80-95	No Change
Cd	40-60	No Change
Pb	1-10	No Change
Se	3-30	No Change
U	70-90	No Change
Ra	5-10	No Change
*F	50-60	10-20

* Approximately 4/10 of input fluorine is found in reactor off-gases and waste gypsum and 4/10 is evolved as SiF_4/HF mixtures during acid concentration.

SOURCE: Lawver (1977).

TABLE 4.19 Percent of Rock Components in Nitric Phosphates

Fe_2O_3	70-90
Al_2O_3	35-75
CaO	40-85
MgO	75-90
Na_2O	80-95
K_2O	80-95
Zn	90-99
Cd	90-99
Pb	90-99
Se	90-99
U	85-99
Ra	5-90
F	40-90

SOURCE: Lawver (1977).

According to EPA (1971) the typical fluorine distribution in phosphoric acid production is as shown in Table 4.20. This is for the dihydrate process of production. The actual amounts of fluorine evolved depend also on the type of rock used and the active silicon-fluorine ratio and many other factors. Therefore, the actual quantities are not strictly stoichiometric.

A few elements have been studied in detail by one or more groups of investigators. For example, fluorine redistribution during wet-process phosphoric acid manufacture has been studied by TVA investigators and there are well-publicized Japanese studies of cadmium movement and of a cadmium-related bone disorder. No specific cadmium compounds have been identified in fertilizer materials. Lehr et al. (1968) have reported that at least 12 fluorine-containing compounds can be isolated from phosphoric acid systems. The fluorine compounds are easily formed and readily identified, but the isolation of trace-element compounds from their surroundings is difficult. Following the flow of many trace elements was not practical before the advent of atomic absorption spectroscopy, and even that tool is not easily adaptable to all problems.

Sulfur is an element that occurs in some ores in greater than "trace" quantities. Its behavior in phosphate systems may not be well understood until good analytical techniques are devised to identify the sulfur compounds that form during processing.

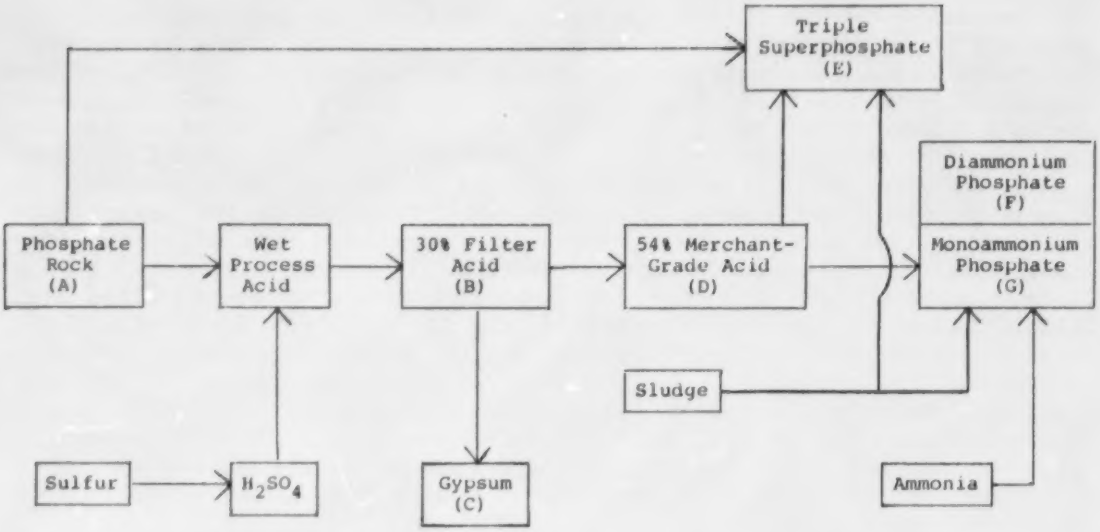
Wet-process acid is used to produce a variety of fertilizer products. The more common products are shown in Figure 4.4. Table 4.21 lists some trace-element concentrations of the various products of a central Florida plant. Mortvedt and Giordano (1977) have presented data on the micronutrient and heavy-metal concentrations in phosphorus fertilizers (Table 4.22 and 4.23).

Fertilizer producers routinely analyze their products for a wide variety of trace elements and heavy metals. Table 4.24 presents a typical routine analysis for granular triple superphosphate; Table 4.25 shows a typical Cd, Cu, Mo, Ni, and Zn analysis for merchant-grade phosphoric acid; and Table 4.26 shows analyses for monoammonium phosphate shipments from a central Florida fertilizer plant.

TABLE 4.20 Fluoride Distribution in Wet-Process Phosphoric Acid Production

Fluoride Disposition	Percent of Total Fluoride in Rock	
	Typical Range	Typical Values
Evolved from Reactor and Filters	4-7	5.5
Evolved from Concentrator	35-45	41.9
Remaining in Gypsum	25-30	27.8
Remaining in Acid Product	20-30	24.8

SOURCE: U.S. EPA (1971).


Triple Superphosphate (E)
Diammonium Phosphate (F)
Phosphate Rock (A)
Wet Process Acid
30% Filter Acid (B)
54% Merchant-Grade Acid (D)
Monoammonium Phosphate (G)
Sludge
Sulfur
H_2SO_4
Gypsum (C)
Ammonia

SOURCE: Lawver (1977).

FIGURE 4.4 Common products of wet-process acid.

TABLE 4.21 Feed and Product Analyses for a Central Florida Plant

Element	A*	B	C	D	E	F	G
Fe %	1.56	1.20	.03	1.57	1.87	2.06	3.59
Al %	1.07	.85	.01	1.44	1.42	1.29	1.83
F %	3.70	2.87	0.39	1.03	2.11	2.53	2.42
Mn (ppm)	407.	375.	33.	679.	557.	589.	34.
Cr "	94.	50.	34.	65.	143.	132.	37.
As "	7.	3.	.04	4.	5.	8.	5.
Se "	2.	.281	.42	.141	1.	2.	1.
Sb "	545.	70.	307.	103.	330.	124.	373.
Pb "	56.	<11.	24.	<11.	43.	<11.	<11.
Cd "	14.	5.	7.	7.	15.	8.	6.
Cu "	11.	3.	5.	5.	19.	8.	6.
Mo "	15.	12.	<15.	21.	15.	30.	<15.
Ni "	83.	24.	46.	43.	62.	47.	43.
Zn "	82.	65.	19.	111.	141.	95.	25.
U "	130.	—	—	240.	200.	220.	160.

SOURCE: Lawver (1977).

TABLE 4.22 Micronutrient and Heavy Metal Concentrations in Phosphorous Fertilizers Made from Phosphate Rock in the Eastern and Western United States

P Source	Origin of PR	Concentration (ppm) in fertilizers							
		Cd	Cr	Cu	Mn	Mo	Pb	Ni	Zn
Ordinary superphosphate	Florida	-	-	28	110	2.7	-	-	55
	Idaho	-	-	49	40	1.8	-	-	417
Triple superphosphate	Florida	-	-	3	220	10.5	-	-	80
	Idaho	-	-	44	40	11.2	-	-	1,040
Ammonium phosphate	Florida	-	-	3	115	2.2	-	-	30
	Montana	-	-	14	100	14.6	-	-	410
Diammonium Phosphate	North Carolina	30	195	1	93	-	5	38	285
	Idaho	50	485	3	195	-	5	64	715

SOURCE: Modified from Clark and Hill (1958) Journal of the Association of Official Analytical Chemists 41:631-637 with the permission of the Association of Official Analytical Chemists and from Mortvedt and Giordano (1975) Journal of Environmental Quality 4(2):170-174 with the permission of the American Society of Agronomy.

TABLE 4.23 Concentration of Phosphorus and Heavy Metals in Phosphorus Fertilizers

P Source	P %	Concentration in fertilizers							
		Zn	Cu	Cd	Cr	Mn	Ni	Pb	V
		ppm							
DAP (reagent)	23.5	1	1.6	0.9	0.2	0.6	1.1	0.5	0.3
DAP (Idaho PR)	20.3	715	2.7	50.0	485.0	195.0	64.0	4.4	1000.0
DAP (N.C. PR)	20.4	285	1.0	30.0	195.0	93.0	38 0	4.7	90.0
10-15-0 (Idaho PR)	15.0	673	1.1	44.0	344.0	125.0	8.0	9.0	1160.0
10-15-0 (N.C. PR)	14.9	500	1.4	17.0	175.0	25.0	35.0	5.2	52.0

DAP = Diammonium phosphate

PR = Phosphate Rock

SOURCE: Mortvedt and Giordano (1977).

TABLE 4.24 Typical Analysis for Granular Triple Superphosphate Shipment

Constituent	Percent
CaO	20.1 - 21.7
Fe_2O_3	1.44 - 1.81
Al_2O_3	1.53 - 1.98
SO_3	1.82 - 2.49
SiO_2	1.35 - 1.78
F	2.22 - 3.03
MgO	0.65 - 0.84
Na_2O	0.29 - 0.35
K_2O	0.082 - 0.105
Organic Matter	0.41 - 0.59
Organic Carbon	0.17 - 0.25
Loss on Ignition (900°C/30 min)	23.5 - 25.1
As_2O_3	0.0005 - 0.0008
Cr_2O_3	0.0120 - 0.0141

SOURCE: Lawver (1977).

Phosphatic animal-feed supplements can be made from defluorinated wet-process acid as well as by thermal methods. The only restrictions on trace-element content at present are:

Wet Acid Specification

F	Not to exceed 1 part F/100 parts P
As	3.2 ppm

TABLE 4.25 Typical Analyses of Merchant-Grade Phosphoric Acid by Shipments (ppm)

Shipped	Cd	Cu	Mo	Ni	Zn	$\%P_2O_5$	%Susp. Solids
1-1-77	8.4	7.9	10.1	30.4	87.7	54.2	1.1
1-18-77	7.0	6.5	9.7	24.8	79.3	53.6	1.3
1-22-77	7.4	7.0	11.2	26.4	76.9	53.8	1.7
1-26-77	5.9	5.9	11.2	25.9	159.1	53.1	1.1
2-9-77	6.5	6.0	11.6	31.4	79.5	53.5	0.8
2-12-77	7.0	6.5	13.9	31.9	130.3	54.5	0.7
2-22-77	4.5	4.5	13.8	26.2	101.6	55.0	1.1
3-4-77	4.5	3.5	12.6	20.9	70.0	54.0	0.5
3-16-77	4.5	4.0	13.1	24.3	69.5	54.1	1.5
3-20-77	4.5	3.5	13.6	24.8	69.2	54.1	1.3

SOURCE: Lawver (1977).

TABLE 4.26 Typical Analyses of Monoammonium Phosphate, by Shipments (ppm)

Shipped	Cd	Cu	Mo	Ni	Zn	%P_2O_5	%N
1-6-77	8.5	5.0	11.5	26.1	72.3	51.0	10.2
1-18-77	5.5	4.0	12.9	14.9	62.5	51.3	10.1
1-27-77	5.0	4.0	15.8	14.8	62.2	51.2	10.0
2-5-77	5.5	5.0	13.5	18.2	74.5	50.2	9.8
2-14-77	7.5	6.0	13.2	20.8	71.1	51.5	10.2
2-20-77	4.9	5.9	12.4	19.8	57.3	50.6	10.3
3-3-77	4.5	5.0	18.1	15.8	67.2	[illegible]	10.2
3-15-77	5.5	5.0	16.0	16.7	57.3	[illegible]	9.7
3-20-77	5.0	5.0	15.9	13.7	67.0	50.6	10.2

SOURCE: Lawver (1977).

Monoammonium Phosphate Specification

F Not to exceed 1 part F/100 parts P

As 1 part As/75 parts P

Heavy metals as Pb 30 ppm

Table 4.27 shows a typical analysis of three samples of defluorinated acid. Solid products made from the acid include dicalcium and monocalcium phosphates as well as diammonium and monoammonium phosphates. Calcination of mixtures of phosphate rock, soda ash, and phosphoric acid also produces defluorinated products useful in the feed industry.

Possible Byproducts from Wet-Process Acid Plants

Phosphate ores, and to a lesser extent the beneficiated concentrates, contain a variety of accessory minerals and elemental constituents which are of commercial interest. Some are unavoidably rejected in mill wastes and chemical byproduct solids, and the processes employed do not lend themselves to economic separations. Most of the metals and rare earths are taken into solution in the phosphoric acid process but are costly to remove. Many accessory elements, therefore, stay with the P_2O_5 and are retained in the finished chemical fertilizers, although some find their way into waste products.

The massive tonnages of rock processed result in large amounts of waste byproducts, notably gypsum and fluorine. If all of these byproducts were recovered they would flood the market and make recovery economics marginal. Some fluorine is recovered, however. The content of impurities, including variable levels of radionuclides, as well as contamination by residual acid, denies a practical outlet for byproduct gypsum in building materials. All these considerations have resulted in a relatively low byproduct recovery rate in most phosphate chemical plants.

TABLE 4.27 Chemical Analyses of Defluorinated Phosphoric Acid

	Sample 1	Sample 2	Sample 3
Total P	24.05%	24.65%	24.53%
Ca	16.3 ppm	19.3 ppm	19.6 ppm
F	0.21%	0.17%	0.15%
Fe	1.92%	2.15%	2.05%
Al	0.93%	0.94%	0.93%
Na	0.029%	0.029%	0.028%
Mg	0.40%	0.41%	0.41%
Si	0.02%	0.03%	0.04%
V	0.014%	0.013%	0.014%
Hg	15.8 ppB	16.9 ppB	14.8 ppB
Cr	115 ppm	108 ppm	106 ppm
As	5 ppm	2 ppm	3 ppm
Pb	1.0 ppm	2.3 ppm	1.5 ppm
Cu	7.0 ppm	6.3 ppm	6.8 ppm
Cd	8.9 ppm	8.9 ppm	9.1 ppm

Solid products made from the acid include dicalcium and monocalcium phosphates as well as diammonium and mono-ammonium phosphates.

SOURCE: Lawver (1977).

Elements in solution with phosphoric acid, with average percent concentration, are as follows (* indicates trace amount) (See also Tables 4.25 and 4.27):

Aluminum (.099)
Arsenic*
Barium*
Boron*
Cadmium*
Chromium*
Copper*
Iron (1.00)
Lead*
Magnesium*
Manganese*
Molybdenum*
Nickel*
Potassium*
Rare Earths*
Silicon (.14)
Sodium*
Strontium*
Sulfur (2.55)
Titanium (.58)
Uranium (.01-.03)
Vanadium (.24)
Zinc*

Rare Earths

The lanthanides and yttrium are present in the apatites found in marine phosphorites and although their concentrations are only in trace amounts, the large volumes of phosphorites treated annually in fertilizer manufacture might make byproduct recovery feasible. The acidulation process in phosphoric acid manufacture completely dissolves the host apatite in which the rare earths occur, and thus the mining, beneficiation, and most of the processing costs for recovering the rare earths are already essentially paid for (Altschuler 1967). However, in view of the potential annual tonnages of rare earths, any substantial recovery effort would lead to oversupply and depress the market value, thus reducing the economic incentives for recovery technology.

Gypsum

The gypsum produced from wet-process acid plants contains some phosphoric acid in the free moisture and some substitution of P_2O_5 in the crystal lattice. Other contaminants include fluorine, trace metals, silica, and acid-insoluble minerals. This gypsum is suitable as a direct application fertilizer-land conditioner (that is, land plaster); however, only about 1 percent of the total wet-process gypsum is required to satisfy this agricultural market. This is the only known use of the gypsum as a byproduct at this time. The remainder is disposed of by stockpiling at the plants.

Use of this gypsum for construction material requires that the gypsum be purified, and this has been shown to be uneconomical. Natural gypsum from Canada readily competes with refined wet-process gypsum even at the phosphoric acid plant location.

As a source of sulfur, gypsum will not be economical until sulfur prices reach very high levels. This does not appear likely in the near future.

Fluorine

Phosphate rock concentrates contain 3 to 4 percent fluorine. Upon production of phosphoric acid a considerable portion of this fluorine is volatilized and released as hydrogen fluoride and silicon tetrafluoride. About 25 percent of the fluorine remains in the product acid, somewhat more than 25 percent goes into the gypsum and the remainder is released as a gas in the form of SiF_4 and HF (see Table 4.20).

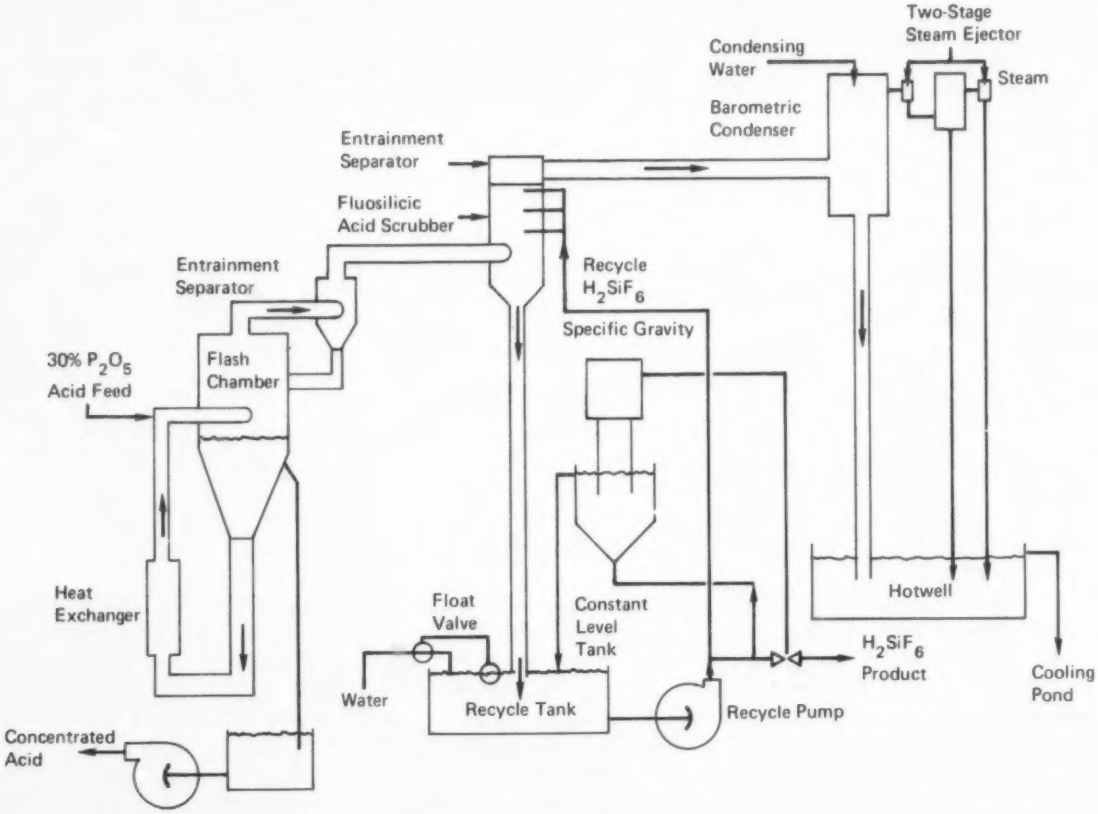
The rock digestion gases released are scrubbed with recycled pond water for emission control and are not usually recovered. In most wet-phosphoric processes only about 35 percent of the fluorine in the rock is available for recovery as fluosilicic acid, because only the fluorine emitted during concentration of the weak acid is scrubbed for H_2SiF_4 production.

Recovery of fluosilicic acid is achieved by scrubbing the vapors from the evaporation where the weak 28-30 percent P_2O_5 acid is concentrated to a strength of 52-54 percent P_2O_5 for use in fertilizer manufacture. Figure 4.5 depicts the most common method of H_2SiF_6 production now practiced in the industry. The evaporator gases are scrubbed with a recycle stream of about 15 percent H_2SiF_6. The acid strength is maintained by removal of strong fluosilicic acid and continuous addition of a small amount of water to the recycle tank. The SiF_4 (gas) is absorbed by the free water (H_2O) to form acid (H_2SiF_6). The process is more complex than shown due to the possible precipitation of silica and the normal use of a three-stage evaporator system. Acid is produced at 15 and 20 to 25 percent H_2SiF_6.

Fluosilicic acid is used primarily for water fluoridation with some going into the production of cryolite. However, Nash and Blake (1977) note that it is also possible to process fluosilicic acid to an acid-grade CaF_2 or to commercially acceptable anhydrous HF. Their report on experimental work of the U.S. Bureau of Mines discusses the treatment of fluosilicic acid with hydrated lime to produce an impure calcium fluoride (called "synthetic fluorspar"), which was found suitable as a substitute for natural fluorspar in some iron- and steel-making operations.

Uranium

All phosphorite deposits of marine origin contain from a trace to increasingly significant quantities of recoverable uranium. The deposits of central Florida are no exception. Typical phosphate ores of the Bone Valley area contain between .007 and .02 percent uranium. The


Two-Stage Steam Ejector
Condensing Water
Steam
Barometric Condenser
Entrainment Separator
Fluosilicic Acid Scrubber
Entrainment Separator
Recycle H_2SiF_6
Specific Gravity
30% P_2O_5 Acid Feed
Flash Chamber
Heat Exchanger
Float Valve
Constant Level Tank
Hotwell
H_2SiF_6 Product
Cooling Pond
Water
Recycle Tank
Recycle Pump
Concentrated Acid

SOURCE: Zellars-Williams, Inc., personal communication (1979).

FIGURE 4.5 Fluosilicic acid recovery.

uranium content of those phosphate deposits generally designated as South Florida are somewhat lower, averaging .005 to .01 percent, but even this quantity has significance as a recoverable resource.

The significance of Florida phosphate rock as a potential source of uranium was first recognized during the 1940s, when the United States ushered the world into the nuclear era. The development of the atomic bomb and the subsequent realization of the potential of nuclear energy as a near-inexhaustible power source resulted in a reassessment of all potential sources for the basic element required--uranium. Consequently, the U.S. Atomic Energy Commission at its Oak Ridge laboratories devoted a great deal of technological effort to developing efficient methods of extracting uranium from naturally occurring sources within the United States. These sources included the phosphate ores being commercially mined in Florida.

Although the assay content of uranium in phosphate rock may seem of little economic significance, it represents, as a rule of thumb, an amount which will yield approximately .8 to 1.0 pounds of recoverable uranium per ton of 100 percent P_2O_5 phosphoric acid produced. Keeping in mind that present United States phosphoric acid production is in excess of 9 million short tons of 100 percent P_2O_5, the minimum amount of potentially recoverable uranium, more than 7 million pounds at a present market value of $40 per pound, is of economic interest. It is not surprising, therefore, that a number of the larger phosphoric acid producers either have initiated commercial recovery or have announced their intentions to construct facilities to recover this valuable resource (see Table 4.28).

Although the chemistry of the uranium-recovery process has been known for some time and is, in fact, part of the public domain, the recovery of uranium from phosphoric acid in an operating complex requires a great deal of technological expertise. Procedures, methods, and equipment which are satisfactory and economical when used to extract uranium from other ores are not usually adequate when applied to a dynamic system such as a phosphoric acid plant, where the primary end product is not uranium but high-analysis fertilizer chemicals.

The basic uranium-recovery process, whether from uranium-bearing ores or from phosphate rock, takes place in three steps:

1. Solubilizing the uranium compounds in the ore.
2. Preferentially extracting the dissolved uranium from solution.
3. Concentrating and refining the uranium extract into a form suitable as a raw material for conversion into fuel.

In the case of uranium extraction from the phosphoric acid, great care must be taken that the extraction process does not hinder the basic production flow or result in damage to process equipment downstream from the extraction acid. Some idea of the magnitude of this problem may be gained by considering that in a modern phosphate chemical complex, the initial stage of the process requires streams having flow rates of 1,000 gallons per minute or more to pass through the uranium-extraction system and return to the main process flow, uncontaminated and essentially unchanged as far as the other production units are concerned.

The first step in any uranium-extraction process is to dissolve the naturally occurring uranium compounds in the ore with sulfuric acid.

TABLE 4.28 U.S. Phosphoric Acid Producers Operating or Constructing Uranium Recovery Facilities

Producer	Annual P_2O_5 production capacity (short tons 100% P_2O_5)	Annual uranium recovery potential (lbs. U_3O_8)
Farmland Industries[1]		
Green Bay, Fla. (planned)	475,000	400,000
Freeport Minerals		
Uncle Sam, La. (production start up 1979)	750,000	600,000
Gardinier, Inc.		
Gibsonton, Fla. (production start up 1980)	500,000	425,000
W.R. Grace[2]		
Bartow, Fla. (current producer)	330,000	264,000
International Minerals and Chemicals Corp.		
New Wales, Fla. (production start up late 1979)	840,000	750,000
Bartow, Fla.[3]	650,000	644,000
Plant City, Fla.[3] (planned)	625,000	616,000
Total	4,170,000	3,699,000

[1] In cooperation with Wyoming Mineral Co.
[2] In cooperation with Uranium Recovery Corp., Mulberry, Fla.
[3] IMCC recovery units at CF Industries' plants.

SOURCE: Zellars-Williams, Inc., personal communication (1979).

This step takes place in a phosphoric acid complex during digestion of the phosphate rock in the attack system. After filtration to remove gypsum and other insoluble impurities, the dilute phosphoric acid-stream containing uranium is subjected to a solvent-extraction process to remove uranium. This is the area where technological innovation is required. The basic solvent-extraction process consists of intimately contacting the dilute phosphoric acid intermediate product after removal of organic matter and pretreatment with a strong oxidizing agent. The extracting solvent is a mixture of di-2-ethylhexyl phosphoric acid (DEPA) and tri-n-octyl phosphine oxide (TOPO) in an aliphatic organic solvent. The uranium compounds are preferentially dissolved in the DEPA-TOPO mixture and, after removal of the organic solvents, the phosphoric acid is returned to the main process stream of the plant. Two areas are extremely critical in this step of the process. First, the dilute acid may contain many contaminants which can hinder the efficiency of the DEPA-TOPO solution. These impurities, principally humic acids and carbonaceous residues, are best removed prior to the solvent-extraction step. This purification procedure is both expensive and complex; however, its successful operation is a principal key to the economic viability of the recovery process.

The second area of critical importance in the extraction phase concerns the removal of all traces of the organic materials used in the extraction process. The aliphatic hydrocarbon used as a solvent for the DEPA-TOPO mix can be extremely destructive to the rubber-lined equipment used extensively in phosphate-manufacturing facilities. The solvent-extraction process cannot be considered acceptable unless the phosphoric acid stream reentering the plant contains less than 70 parts per million of organic materials.

After completion of the critical solvent-extraction step, concentration and purification of the separated uranium is fairly straightforward. It is usually carried out using established procedures developed by the uranium-mining industry.

The final product of this process is obtained by precipitating the uranium from the final solution, either as ammonium uranyl tri-carbonate (AUT), using concentrated ammonium carbonate as the active reagent, or through the use of hydrogen peroxide to obtain the hydrated peroxide salt, $UO_4.2H_2O$. The latter material, known as "yellow cake," is the most common form of uranium supplied to upgrading facilities for refining into fuel for nuclear reactors and for other purposes.

The present value of yellow cake, ranging from $40 to $43 per pound for spot sales to $28 to $40 per pound on existing, long-term sales arrangements, makes the recovery process an interesting possibility for wet-process phosphoric acid producers. However, the complexity of the extraction process, as well as the cost of some of the specialized equipment involved, is a deterrent to the small operators.

Present capital investment in a complete facility capable of extracting the uranium values from a phosphoric acid stream and converting them to marketable "yellow cake" will run between $75 and $110 per pound of uranium recovered per year. Thus, a uranium-recovery project undertaken by a producer having P_2O_5 production capacity of some 250,000 short tons per year would represent an investment of $25 million to $30 million. Assuming a 12-year plant life, this investment would equate to a fixed cost of more than $8 per pound of yellow cake produced. Coupled with the high cost of some of the more exotic process reagents required (for example, TOPO, at a present value of $7 to $8 per pound) and the level of maintenance required by a complete uranium-recovery complex, production costs can be expected to range between $20 and $25 per pound of yellow cake produced. In spite of these high costs of production, the present and future market projections for uranium make this investment attractive, at least for the larger and more financially able phosphate producers.

In addition, the "clean-up" of the diluted phosphoric acid stream which takes place during the uranium-extraction phase provides a better quality material to the downstream units at essentially no cost. This fact could be of very significant economic importance to phosphoric acid producers in the future as they are forced to use lower-grade, less desirable phosphate ores.

Indications are that some of the undesirable constituents of these ores can be removed at little additional cost during the uranium-extraction step; however, much of this work is in the preliminary stages and will require further development before its economic practicality is clearly established.

DISTRIBUTION OF NONPHOSPHORUS CONSTITUENTS IN THE PRODUCTION OF ELEMENTAL PHOSPHORUS

The following discussion of the production of elemental phosphorus and the associated redistribution of accessory elements is based on the presentation by Barber (1977) at the NAS workshop on phosphate rock accessory minerals.

Phosphorus Production

Phosphorus is produced by smelting a mixture of phosphate rock, silica rock, and coke in a submerged-arc electric furnace. Silica rock supplies the SiO_2 needed to combine with the CaO in the phosphate rock. The resulting calcium silicate is the principal constituent of the slag. Coke supplies the carbon required to reduce combined phosphorus to the elemental form. Table 4.29 shows the typical quantities of material processed to make phosphorus.

Other Products

Slag

Most of the nonphosphatic material charged into the phosphorus furnace comes out in the slag. This includes various metal oxides from the phosphate rock, silica, and coke ash that remain unreduced by smelting. About 8.4 tons of silicate slag are obtained per ton of phosphorus produced; the composition of the slag is shown in Table 4.30.

In the past, crushed and sized slag has been used as ballast and as an aggregate. At one time, the Tennessee Valley Authority (TVA) produced an aggregate material by quenching molten slag with a water-jetting technique to form granules less than 10 mesh in size. The granulated slag was used to make concrete blocks and for other purposes where it could be substituted for sand-size materials. However, because of the radioactive constituents, phosphorus slag granules are no longer used in building materials. TVA also produced at one time an experimental aggregate by foaming the furnace slag into an expanded light-weight material.

TABLE 4.29 Typical Quantities of Raw Materials Smelted in Making One Ton of Phosphorus

Material	Tons
Phosphate rock	9.5
Silica rock	1.7
Coke	1.5
TOTAL	12.7

SOURCE: Barber (1977).

TABLE 4.30 Typical Analysis of Major Constituents of Slag

Constituent	Percent
CaO	44.1
SiO_2	41.3
Al_2O_3	8.8
P_2O_5	1.3
F	2.8
K_2O	1.2

SOURCE: Barber (1977).

In some places granulated slag, which is an alkaline product, has been used instead of limestone to treat acid soils. However, because the Al_2O_3 content must not exceed about 7 percent for this use, slag produced from low-grade phosphate rock is precluded.

Ferrophosphorus

Iron oxide in the phosphate rock and coke ash is reduced in the phosphorus furnace to elemental iron, which combines with phosphorus to produce an alloy mixture of iron phosphides--Fe_3P, Fe_2P, FeP, FeP_2--known collectively as "ferrophosphorus". About .3 ton of ferrophosphorus is obtained per ton of phosphorus. The quantity may vary from .1 to .4 ton depending on the iron-oxide content of the phosphate rock smelted, since about 90 percent of the iron comes from the phosphate rock.

A typical analysis of ferrophosphorus, obtained when a mixture of Tennessee and Florida phosphate (about 75 percent and 25 percent, respectively) was smelted, is given in Table 4.31. Ferrophosphorus has a variety of uses in the iron and steel industry. For these uses, the phosphorus content should be as high as possible (20 to 26 percent) and the silicon content should be less than 2.0 percent. According to Burt and Barber (1952), the byproduct ferrophosphorus sold to the metallurgical industry consists mainly of Fe_2P and a richer phosphide.

TABLE 4.31 Typical Analysis of Ferrophosphorus

Constituent	Percent
Fe	68.8
P	24.0
Si	1.7
Mn	1.1

SOURCE: Barber (1977).

Precipitator Dust

Particles in the furnace gases are removed by electrostatic precipitation prior to the recovery of phosphorus vapor by condensation. About 150 pounds of precipitator dust is obtained per ton of phosphorus produced. The dust has the following composition: 29 percent P_2O_5; 16 percent K_2O; 18 percent SiO_2; 11 percent CaO; and 6 percent F. Some precipitator dust has been sold as a byproduct to recover the fertilizer values (P_2O_5 and K_2O). Domestic phosphate ores contain zinc in the range of 100 to 300 parts per million. Precipitator dust from these ores may have some value as a source of this micronutrient.

Coke Dust

When coke is dried, some of it is entrained in the exhaust gases. The entrained coke particles must be removed from the gases to prevent air pollution. The collected dust is ordinarily burned or otherwise disposed of as a solid.

Distribution of Some Accessory Constituents

Fluorine

When a mixture of Tennessee and Florida phosphate rock is smelted, about 597 pounds of fluorine will be produced per ton of phosphorus. Calcination at a temperature of about 2,200°F drives off about 50 pounds of the fluorine; about 525 pounds will go into the slag; and a small amount (about 22 pounds) will be volatilized from the phosphorus furnace and will go into the precipitator dust, phosphorus sludge, and condenser-spray liquor. Only about 64 pounds of fluorine per ton of phosphorus is available for recovery as a byproduct.

Much larger amounts of fluorine are volatilized when phosphate is calcined at higher temperatures: as much as 225 pounds of fluorine may be available for recovery if the phosphate is nodulized at a temperature of about 2,600°F. Information about the distribution of fluorine and the potential for its recovery as a byproduct has been presented by Barber and Farr (1970).

Vanadium and Chromium

Compounds of vanadium and chromium occurring in the phosphate rock are reduced in the phosphorus furnace to the metals that go into the ferrophosphorus. Ferrophosphorus produced in the smelting of phosphate ores from Florida or Tennessee contains less than .1 percent vanadium or chromium, but ferrophosphorus from smelted western phosphate ores may contain 3 to 5 percent vanadium and chromium (Banning et al. 1953). Processes for recovery of these metals from the byproduct ferrophosphorus have been described (Darrow 1964).

Germanium and Gallium

Coke contains small amounts of germanium and gallium, which go into the precipitator dust--about 530 parts per million (ppm) of germanium and 100 parts per million of gallium (Waters and Kenworthy 1967). It has been reported that at one plant precipitator dust is sold for its gallium content (Lott and Womer 1974).

Uranium

Phosphate rock of commercial grade contains 100 to 200 parts per million uranium, the content generally increasing with the P_2O_5 content of the ore. When phosphate rock is smelted, the uranium goes into the slag and offers a potential source for recovery. Young and Altschuler (1958) found that the pseudowollastonite slag from smelting of phosphate rock contained 180 parts per million of uranium and that great enrichment occurs in ferrophosphorus inclusions in this slag. The inclusions were found to have 650 parts per million of uranium. Young and Altschuler also suggested some recovery methods for this uranium. Radon-222, a daughter of radioactive uranium, also goes into the slag. The distribution of radioactive materials resulting from the smelting of phosphate rock has been reported by Guimond and Windham (1974).

POTENTIAL ENVIRONMENTAL HAZARDS

The redistribution of accessory elements associated with the mining, processing, and use of phosphate materials has potentially adverse effects on the environment--that is, on plants, animals, and man. The pathways of these elements into the environment are primarily through atmospheric emissions and process water in the chemical treatments applied to phosphate rock products, and secondarily through the application of fertilizers to the soils. Two elements, namely fluorine and uranium, are of particular concern to man because of possible damaging effects on human health. However, it is not the objective of this discussion to treat health problems that might result from the redistribution of accessory elements, but rather to point to redistribution pathways and provide an alert to potential health hazards.

Redistribution of Accessory Elements in Atmospheric Emissions and Process Water

Mining

The mining process consists of stripping away the overburden with a dragline and depositing this material in a mined-out cut. After sufficient matrix (ore-bearing material) has been uncovered, the same dragline digs the matrix and places it in a slurry well to be pumped to the plant. These processes do not in themselves create airborne particulate emissions, since the materials being handled are usually in the range of 15 to 25 percent moisture and dust is not created. During the dry season mine roads can create some airborne emissions; however, this is relatively minor. The question of release of radioactive materials to the atmosphere by the route of dust has been discussed extensively during the last 2 years and this subject is still under study. Very safe working levels are reported, however, and thus radon is not considered a problem in the mine area.

The most highly radioactive material in the mining operation is usually in the leach zone near its contact with the underlying matrix. This material, although high in P_2O_5, is usually wasted with the overburden in the spoiling process. This radioactive material can be readily covered with overburden so that after reclamation it is not exposed.

The uranium and other radionuclides plus the fluorine contained in the matrix are in a water-insoluble state and are therefore not a potential hazard as far as contamination of water or air, except in the form of particulate emission. The long-term decay habits of radium-226, forming radon gases, do create some airborne radioactivity. However, these concentrations are not sufficient to cause working condition hazards as the half-life of radon is very brief.

Beneficiation

Processing of the matrix is conducted in a wet state and no hazardous chemicals are employed. The reagents used in flotation are not employed in large quantities and by nature of the process finally report to the clays, where they are adsorbed and neutralized without appearing in waste water. Since no chemical alteration of the minerals occurs in the process, the minerals remain essentially water-insoluble and are not distributed to the environment.

Rock Drying

The method of treating phosphate matrix to produce phosphate rock does not involve drying the material until the product has been upgraded to a point sufficient for shipment. At that point some of the rock is dried before shipping. Recent developments in processing phosphate rock have taken advantage of wet-rock grinding and feeding this wet rock directly into the phosphoric acid process without drying.

The drying process removes water in a fluid-bed dryer. Dust is collected in cyclones and wet scrubbers. Recently, EPA guidelines placed severe restrictions on the construction of new dryers, requiring that specific justification be presented for the dry rock before drying would be permitted.

Mine Waste Disposal

The solid wastes from a phosphate beneficiation plant consist of clay slimes and sand tailings. These waste materials are usually deposited in separate areas for dewatering and eventually used for land reclamation. The amount of radioactive materials in the waste varies broadly, depending on the type of ore that was mined and the degree of efficiency in processing the ore. However, in general the uranium content of the waste is in proportion to the BPL content. Therefore, in some of the richer slimes higher concentrations of uranium occur in the fine phosphate fractions. To a certain degree, the fine phosphate particles will settle to the bottom of the clay pond; however, the dynamics of these ponds as to radioactivity are not fully documented. The sand tailings are quite low in uranium content. Recent developments in mixing of the sand and the clay, in order to create a more stable land reclamation mix, have resulted in a reduction of the radioactive material content of the waste. This procedure is being adopted, especially in new mines, since the ratio of sand to clay is very favorable for this process.

Older mining areas, where large volumes of clay slimes exist, could present a problem because of the presence of uranium and radioactive materials near the surface. However, in most cases the minerals containing the BPL, and consequently the uranium, have concentrated in the bottom of the slime pond due to settling of the fine phosphate particles. It is normal to reclaim land by covering with as much overburden as possible to promote a more stable, useful reclaimed land. This technique, of course, reduces the hazards of radon emissions since a cap of overburden retards the release of radon gas to the atmosphere.

All these factors are being considered in detail by the phosphate industry, the EPA and the Florida State Board of Health. Precautions have been recommended, such as capping with overburden and using construction techniques for ventilation of foundations to avoid radon buildup in structures. The radon distribution has not been adequately defined and is still presently under study. It has been shown that some areas of outcrop of matrix or leach zones occur naturally in the central Florida area and attention to this type of problem is not restricted entirely to the phosphate industry.

Mine waste water which may be discharged into surrounding streams is another potential source of escape of undesirable elements into the surrounding area. The water released from phosphate mines and discharged to local streams is usually of high quality and does not contain a significant quantity of fluorine, P_2O_5, or radium-226. Table 4.32 shows data collected by the EPA of typical central Florida phosphate mine discharge water. Fluorine, P_2O_5, and radium-226 may occur in water due to suspended solids which are rich in BPL content. The practice is to ensure that water discharged is low in suspended solids. Requirements for discharge-water quality are, therefore, not difficult to meet. The requirements for discharge-water quality are outlined in Florida Statutes Chapter 17-3, Department of Environmental Regulation, and in Rules and Regulations of the U.S. EPA Part 436, Mineral Mining and Processing Point Source Category.

Rock Transportation

The transportation of phosphate rock in the wet form presents no environmental problem since there is no dust problem. The transport of

TABLE 4.32 Average Water Quality Discharge Values, Central Florida Phosphate Mines

Plant No.	Total Discharge Liters/Metric Ton	Effluent Characteristics					
		Total Suspended Solids Kg/Metric Ton	Total Suspended Solids Mg/1	Phosphorus Total Kg/Metric Ton	Phosphorus Total Mg/1	Fluoride Kg/Metric Ton	Fluoride Mg/.
4016	262	-	9	0.0003	1.2	0.0005	1.9
4002	335	0.003	9	0.006	1.8	0.0006	1.8
4019B	720	0.007	10	0.0013	1.8	0.0012	1.7
4019A	960	0.008	8	0.0016	1.7	0.0017	1.8
4005C	1,400	0.046	33	0.007	0.5	0.0022	1.6
4019C	1,680	0.016	10	0.0018	1.1	0.0054	3.2
4020B	2,530	0.017	8	0.0028	1.1	0.0078	3.1
Average	893 (214 Gal/ST)		13		1.3		2.2
Std. Dev.	569		9.8		0.5		0.7

SOURCE: U.S. EPA (1975).

dry phosphate rock is carried out in closed hopper cars. Fugitive dust control at loading and unloading points is required.

Chemical Processing

The uses of phosphate rock are shown in Figure 4.6. The major product categories, byproducts, and wastes are:

Products
- Direct application rock
- Phosphorus (miscellaneous uses)
- Sodium phosphates (detergent use)
- Furnace phosphoric acid (miscellaneous uses, including fertilizers)
- Animal feed phosphates
- Defluorinated phosphate rock and derivatives (feed ingredients)
- Normal superphosphate (fertilizer)
- Triple superphosphate (fertilizer)
- Ammonium phosphates (fertilizer)
- Liquid fertilizer (fertilizer)
- Feed phosphates by wet-process acid

Byproducts
- Furnace slag
- Ferrophosphorus
- Fluosilicic acid
- Uranium

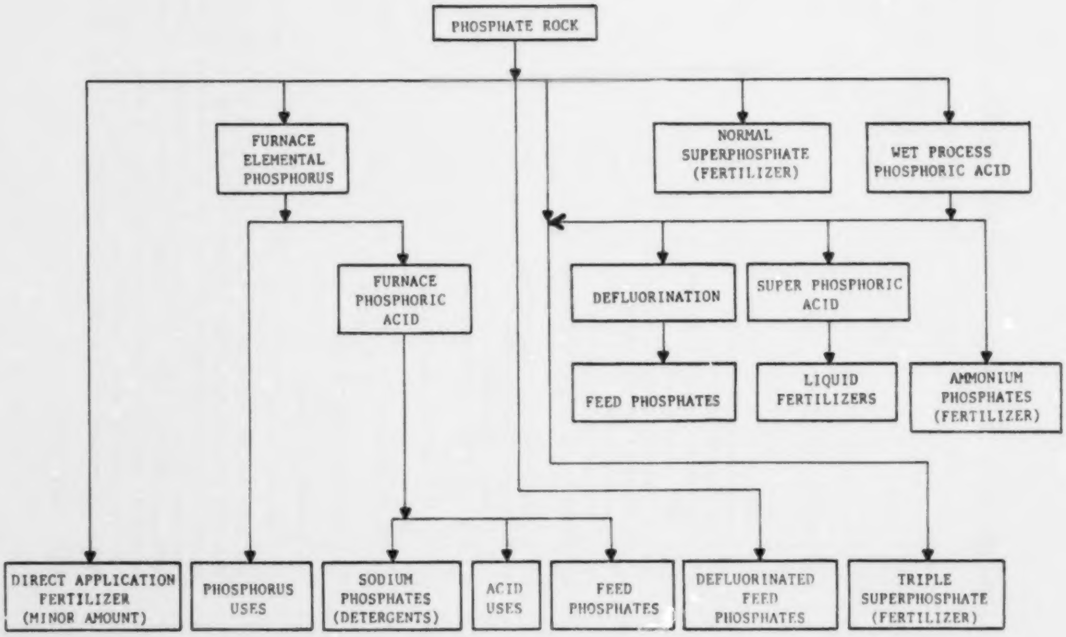
Wastes
- Gypsum
- Unrecovered byproducts

Most of the phosphate rock in the United States is processed through wet-process phosphoric acid plants where the main mobilization of accessory elements such as fluorine and uranium occur.

Fluorine

U.S. phosphate ores commonly contain 3 to 4 percent fluorine, and thus the large-scale mining of phosphate rock--about 47 million metric tons in 1977 (Stowasser 1979)--can result in the production of an enormous quantity of fluorine. According to Lehr (1978) fluorine mobilized in the mining and processing of phosphate rock must ultimately be accounted for either in (1) contained waste products (both solid and liquid); (2) losses to the environment through volatile emissions, process water storage-pond overflow, and underground seepage; (3) recovered as a byproduct; or (4) in manufactured products (notably fertilizer). He has shown the distribution of fluorides in ore processing from four industrial plants in Florida (see Table 4.33). These fluoride balances are first approximations based on the best available analytical data, and are subject to refinement when more comprehensive analytical data become available.

Solid-waste products, primarily gypsum cake precipitated in the acidulation of phosphate ores, contain substantial quantities of associated fluorides. Some of these fluorides, such as CaF_2, are relatively stable and insoluble. Others have relatively high


PHOSPHATE ROCK
FURNACE ELEMENTAL PHOSPHORUS
NORMAL SUPERPHOSPHATE (FERTILIZER)
WET PROCESS PHOSPHORIC ACID
FURNACE PHOSPHORIC ACID
DEFLUORINATION
SUPER PHOSPHORIC ACID
FEED PHOSPHATES
LIQUID FERTILIZERS
AMMONIUM PHOSPHATES (FERTILIZER)
DIRECT APPLICATION FERTILIZER (MINOR AMOUNT)
PHOSPHORUS USES
SODIUM PHOSPHATES (DETERGENTS)
ACID USES
FEED PHOSPHATES
DEFLUORINATED FEED PHOSPHATES
TRIPLE SUPERPHOSPHATE (FERTILIZER)

SOURCE: Zellars-Williams, Inc., personal communication (1979).

FIGURE 4.6 Phosphate rock uses.

TABLE 4.33 Fluoride Chemical Distribution Balances (normalized to 1,000 tpd P_2O_5 Production)

	Company A		Company B		Company C		Company D	
	Process material	F content	Process material	F content	Process material	F content	Process material	F content
Accountable Fluoride								
1. F to waste streams:								
Gypsum cake (total solids)	5182	25.70	5169	31.02	5370	22.55	5261	33.83
Stacked water (process water)	2221	19.99	2215	6.86	2302	13.58	2255	14.65
2. F to byproduct H_2SiF_6	0		22.30	17.64	0		33.59	26.58
3. F to manufactured products:								
Wet process acid (direct sales)	0		376.6[b]	3.20[b]	0		525.5	4.78
Granular triple superphosphate	0		428.6	10.16	2129	50.02	719.1	18.05
Diammonium phosphate	2174	37.50	1142.9	24.11	0		821.9	1504
4. F uptake by replaced process water[c]	4401	39.61	4176.5	12.95	4659	27.50	(3446)	(22.40)[d]
5. F uptake by recycled seepage	N.A.[e]	N.A.	2625	8.14	N.A.[e]	N.A.	N.A.	N.A.
6. F removed from process water discharge	0		0		0		1235	8.03
7. F as allowed stack emissions[f]		0.162		0.143		0.162		0.149
Total (accountable)		122.96		114.22		113.81		121.11
F Input (Feed Rock)		122.63		118.29		115.51		120.86
Net F (unaccountable)		(-0.33)		+4.07		+1.70		(-0.25)
percent of total		0		3.56		1.47		0

[a] All data values reported as tpd adjusted to a normalized production rate, based on actual rock input and production rate.

[b] Weighted mean of materials composite (feed rock or products).

[c] Based on the steady-state composition of process water systems relative to water and fluoride balances.

[d] Accounted elsewhere in this positive water balance system; net process water makeup of 3446 tons [4681 t total (0% F) minus 1235 t overflow (0% F)], with an F uptake capacity at pond equilibrium (6500 ppm F) equal to 22.40 t F, corresponding to F removed from stacking water plus lime-treated overflow (22.68).

[e] Data on quantity and composition of recycle not available for inclusion.

[f] Based on percent of allowable maximum stack emission actually released.

SOURCE: Lehr (1978).

solubilities and may be dissolved and recycled in process waters. However, solid fluorides are generally contained within the processing and storage-pond system.

More important are liquid wastes, which have a greater potential than solid wastes for escape into the environment. In wet-process phosphoric acid manufacture, the sulfuric acid treatment of phosphate mill feed results in waste liquors containing sodium and potassium fluorosilicates, hydrofluoric acid and fluosilicic acid, which accompany gypsum slurries to large settling ponds. Recirculation of process waters may result in an increase in the concentration of hydrofluoric and fluosilicic acid, but generally the acids are contained within the processing system. When release of excess waste water is necessary, the acids are neutralized and controlled through a two-stage lime treatment process.

Although most of the fluorine in processing operations is contained in one form or another, the potential for leakage into the environment exists. Stack emissions in the processing of phosphate ores contain significant amounts of fluorides, which are removed by efficient scrubbing. However, some escape to the atmosphere may occur, although control systems for removal of fluorides are very effective. The amounts of fluorides released in stack emissions are small (See Table 4.33). Very careful monitoring of industrial-plant emissions is carried out at many plants so as to identify and mitigate any serious pollution problems. In addition to stack emissions, atmospheric emission of fluorine from storage-pond waters does occur, and in fact this latter is probably the principal source of fluorine escape to the atmosphere (NRC 1971). Stringent regulations now require careful control of fluorine emissions, but the potential for environmental pollution and resulting health hazards has not been totally eliminated.

Seepage of pond waters into surrounding soils and possibly into water-supply formations is a major environmental concern. Because of this, the containment systems in modern plant facilities are designed to minimize any leakage potential. Even if leakage occurs, limited data available (Wissa 1977) suggest that percolation rates of water through gypsum cake in settling ponds and underlying clayey sediments in parts of Florida will be very low. In addition, for any contaminated waters that might escape, geologic formations with abundant clays and carbonate minerals would provide a further filtering effect, by reacting chemically with fluoride-bearing waters to immobilize fluorine and certain other elements (see Lehr 1978). There is, however, some danger, though small, that heavy rains may cause overflow of fluoride-bearing waters from storage ponds and that some contamination of soils as well as of ground and surface waters might occur locally in the vicinity of processing plants. The controlled release of treated pond waters and storage-pond design to accommodate unusually severe storm events, however, combine to minimize this potential hazard. There is, of course, always the possibility, however remote, that an accident, such as failure of confining banks of storage ponds, could result in substantial short-term fluoride pollution of the environment. One need only note the large amount of fluorine generated annually in the mining and processing of phosphate rock--over 1 million tons--to appreciate EPA's stringent regulations on fluorine losses.

Emission Control Measures In the mining operations the major source of emissions is dust from unpaved roads and from rock drying and dry-rock loadout. The drying and loadout systems limit the emission of particulates by the use of dust collection and scrubbing systems. In Florida these point sources and fugitive dust emissions are closely controlled by the State Department of Environmental Regulation.

Emissions from processing operations vary with the product being produced, but limiting standards have been set for all phases of processing activity. In the production of wet phosphoric acid, emissions of fluorine from new plants are restricted to approximately .02 pound of fluorine per ton of rock P_2O_5 fed into the system. For existing plants and other processes the limits are somewhat higher. Restricting emissions is accomplished by the use of scrubbers on the attack and evaporation systems. The fluorine, which is evolved as SiF_4 and to a small extent as HF, is collected in the scrubbers and sent to the chemical-plant cooling pond. In these ponds recirculation of water is accomplished to remove heat and to absorb the fluorine emission. These ponds are chemically balanced so that, as fluorine is added from the scrubbing system, precipitation of solid fluorides occurs. Emission of fluorine from cooling ponds is still under study. The details of the chemical process which takes place in the scrubbers' pond are not completely understood at this time.

Discharge of water from the phosphoric-acid-plant cooling ponds and gypsum storage areas is closely controlled and limited by the EPA. The quality of the water from these ponds must meet strict specifications for P_2O_5 and fluorine content. Those companies which can properly balance their ponds do not discharge waste waters. In cases where discharge is necessary it is accomplished only after extensive treatment of the pond effluent with limestone and calcium hydroxide to reduce the P_2O_5 and F to EPA standards.

Emissions from diammonium phosphate plants, calciners, and other fertilizer chemical plants are also closely monitored as point sources and emissions controlled by the use of scrubbers.

In the past one of the major sources of fluorine emissions was from curing sheds used in the Run-of-Pile triple superphosphate process. The difficulty of controlling emissions from these large warehouses has to some degree influenced further production of this product and in many cases companies have eliminated production of the Run-of-Pile triple superphosphate. Those companies still producing triple superphosphate have installed extensive scrubbing systems on the curing sheds in order to meet emission standards.

Granular triple superphosphate, which is produced by a different process, has replaced the conventional triple superphosphate, since the granular process allows the scrubbing of the waste gases and effective control of fluorine emission.

Uranium

Uranium is present in marine phosphorites in amounts averaging about .01 percent and may be of some environmental concern in the mining and processing of phosphate rock. Radon-222, a product of radioactive decay of uranium-238, is redistributed when the phosphate beds are mined.

Prior to mining the overburden provides a protective shield against radiation and from decay products. Stripping operations, however, may mix the overburden with some uranium-bearing waste rock, thus resulting in contaminated spoil piles. Radium-226 may exist in reclaimed surface and near-surface soils at activity levels up to 10 times those normally found in U.S. surface soils, and, although many do not consider the radioactive contamination to be significant, the decay of radium-226 could produce radon gas that might be detrimental to the use or habitation of areas underlain by these soils. This is especially true for some earlier-mined areas where the most uraniferous waste material at the base of the overburden has been piled on top of the ground. The potential severity of radon contamination from phosphate mining is not fully known,but radioactivity surveys might be useful in delimiting those areas that should be avoided for housing, farming, recreation, and other uses.

Uranium and its decay products may also be redistributed through processing wastes. About 60 percent of the uranium values in the matrix are recovered in the pebble and concentrate products; most of the uranium losses occur in the slimes.

Fate of Nonphosphorus Constituents of Phosphate Fertilizers Applied to Soils

Mortvedt and Giordano (1975) pointed out that all phosphate rock contains various heavy metals and essential plant nutrients as accessory elements. Some of these constituents may be lost during processing, but most of the heavy metals are retained in wet-process phosphate fertilizer. They are thus applied to the soil, where they may be absorbed by plants, retained by the soil, or leached into ground waters. Those absorbed by plants may enter the human food chain.

Because the concentrations of heavy metals in phosphate fertilizers are generally quite low, their accumulation is not significant at normal rates of application of the fertilizers. For example, the amount of a heavy metal that would accumulate in soil would probably be no more than about 2.5 pounds per acre if phosphate fertilizer containing 50 parts per million of that metal were applied at a rate of 500 pounds per acre annually for 100 years and none was leached. It would be desirable to develop firm data based on long-range studies of accessory element accumulation in soils.

In general, the uptake of heavy metals by plants is lower than the uptake of secondary nutrients and micronutrients. Thus, application of some heavy metals as accessory constituents in fertilizers may not result in increased concentrations in plants. Most of the information in the literature concerning uptake of heavy metals by plants has come from experiments in which heavy-metal salts or municipal wastes containing heavy metals have been applied to soils. Predictions of the fate of the heavy-metal constituents after phosphate application to soils may be inferred to some degree from the results of those experiments. But the long-term cumulative effects of fertilizer applications and resulting plant uptake of heavy metals and other trace elements will be known only after careful long-term studies have been undertaken.

According to the Council for Agricultural Science and Technology (CAST 1976) the elements in sewage sludge fall into two categories--those that do and those that do not represent a potentially serious hazard to plants or animals when applied to cropland. The elements that constitute a relatively small hazard are Mn, Fe, Al, Cr, As, Se, Sb, Pb, and Hg; the elements constituting a potentially serious hazard are Cd, Cu, Mo, Ni, and Zn. These conclusions are based on numerous plant-uptake tests described in detail in the CAST report. It is particularly interesting to note that three of the potentially hazardous elements--copper, molybdenum, and zinc--are also micronutrients.

Phosphate fertilizers may also contain small amounts of radioactive uranium, radium, and thorium. Concern has been expressed that these elements may be absorbed by plants, become part of the food chain, and ultimately enter the human body. In general, plant uptake of these elements is low, and little is known of their reactions in soil.

The Department of Agriculture is conducting a large and continuing research effort concerning the fate of non-phosphorus constituents applied to soils. The existence of this program is encouraging, though much is still to be done.

CONCLUSIONS AND RECOMMENDATIONS

The phosphate rock deposits of the future in the United States will resemble those currently being mined, with gradual changes in grade and composition. In general, the BPL content of the deposits will be lower and the content of carbonate minerals will be higher. The uranium content of the product will, for the most part, also be lower. Beneficiation techniques will be similar to those now in use, but a third stage of flotation will be required to reduce the carbonate mineral content to the level at which the MgO content in the concentrates will not exceed about 1 percent. The types of accessory minerals that will be encountered will be the same as those encountered in present operations. The grade of the flotation concentrate will be several BPL units lower than that of current production.

Severe unsolved problems that will affect accessory constituent content and redistribution are those of how to mine deposits covered by considerably thicker overburden and deposits that are much deeper than those currently being mined. The mining problems, coupled with the still unsolved slime-disposal problems, will be the major technical challenges facing the industry in the future.

Much information is already available about the redistribution of accessory elements from the phosphate rock concentrates through various fertilizer and chemical products, and a large amount of additional research is being carried out by various government agencies. This research must be continued, as much must still be learned about the uptake of trace elements by plants and about the chemical forms and possible reactions of trace elements in the manufacture of fertilizer. We particularly need a better understanding of the long-term and potentially deleterious effects of continuous fertilization of intensely farmed areas, both in terms of fixation and of redistribution of trace elements in and through the soils and in plant uptake.

There are very few guidelines concerning the disposition and handling of accessory elements in the various fertilizer products. However, the Association of American Feed Control now has an active program to develop such guidelines for animal-feed products, and the National Academy of Sciences Subcommittee on Mineral Toxicity in Animals is carrying out an extensive program to develop guidelines for trace elements allowable in animal feeds. CAST has already issued reports about the potential hazards heavy metals might present to plants and animals through the application of sewer sludge to croplands, and the U.S. Department of Agriculture has numerous research projects concerned with the uptake of trace elements in various types of crops. The phosphate industry has provided a grant to the University of Florida to evaluate the effects of radon and to make recommendations regarding acceptable methods of using phosphate waste for reclaiming land.

The U.S. Bureau of Mines has proposed a process of direct acidulation to alleviate the slime problem. It is the Panel's view, however, that the low-BPL slime ores of the future (6 percent BPL) and the high carbonate matrix will preclude practical use of direct acidulation.

The principal areas that deserve governmental and industrial effort and support appear to be: (1) developing new technology to permit mining the deeper deposits economically; (2) recovery of uranium and fluorine associated with the phosphate deposits; (3) developing ways to concentrate the rare earth elements contained in the phosphate deposits; and (4) continuing research into the social significance and possible environmental problems associated with the redistribution of the heavy metals and trace elements that occur in phosphate rock and, in particular, of those associated with processing in phosphoric acid and fertilizer plants.

In general, the phosphate industry is conscientious about obtaining chemical analyses of both ore concentrates and subsequent phosphate chemical plant products, but the industry lacks realistic guidelines from the federal government concerning environmental and trace-element control.

The U.S. Department of Energy has authorized an extensive study of the occurrence of uranium in phosphate in the United States. This study is presently under way, with the objective to identify the potential sources of uranium within phosphate deposits in Florida, the southeastern United States, Tennessee, and in western phosphates. This will be a detailed evaluation and should provide considerable information on the occurrence of uranium in ore to be mined in the future.

There is a need for additional information on the redistribution of uranium and other radioactive materials in the fertilizer processes for the purpose of defining economical ways of recovering these products. There is also a need for information on the redistribution of radioactive materials in mining and process wastes, as a basis for assessing potential health hazards of reclaimed or reclaimable lands. In this regard radiometric surveys of habitable or arable areas where gypsum wastes, slimes, and leached-zone materials are exposed should be made routinely.

Recovery of heavy minerals from phosphate ore is uneconomical by present technology and market conditions. As a result large tonnages of these minerals are lost annually. Improved technology could be a useful incentive for recovery. Secondary benefits of improved phosphate rock grade would also result.

There is presently little economic incentive for recovery of rare earths from phosphate ores. More study of removal of these elements and their market potential is needed.

The recovery of fluorine is strictly limited by market demand and economics. The technology for recovery exists. Increased research in the production of fluorine products, such as calcium fluoride to replace imported fluorspar, is indicated. Production technology for fluorine compounds and products needs particular attention.

The list of products which may be produced from phosphate slimes and/or sand tailings is extensive. The problem has always been the cost of drying the clays from 18 percent solids to about 50 percent solids (natural clay). Development of satellite industries based on phosphate clays may be possible with improved technology developed in slimes-disposal investigations.

The comments for slimes apply to gypsum, but with the qualification that radium must be removed before gypsum is used for building materials. Natural gypsum from Nova Scotia is presently being imported into the southeastern United States at a cost of $10 per ton, a price with which byproduct gypsum from phosphate ores presently cannot compete.

The importance of trace elements and secondary nutrients for plant growth should not be overlooked. Phosphate rock does supply some of the compounds necessary for healthy plant growth. This area may require better definition, both of negative and positive aspects.

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APPENDIX:
TECHNICAL PROGRAM OF WORKSHOP ON ACCESSORY MINERALS IN PHOSPHATE ROCK

The Workshop on Phosphate Rock Accessory Minerals, organized by the Phosphate Panel of the Committee on Accessory Elements, National Research Council, was held on February 24-25, 1977, at the National Fertilizer Development Center of the Tennessee Valley Authority, Muscle Shoals, Alabama. The technical program was as follows:

Patterns of Phosphate Rock Production and Use
    J.R. Douglas and E.A. Harre, TVA National Fertilizer Development Center
Reserves and Resources of Phosphate in the World with Special Reference to the United States
    James Cathcart, U.S. Geological Survey
Accessory Minerals in Phosphate Rock
    G.H. McClellan, International Fertilizer Development Center
Rare Elements in Phosphate Rock of Southeastern Idaho and Phosphate Reserves in Southeastern Idaho
    R.A. Gulbrandsen, U.S. Geological Survey
Accessory Elements in Phosphorites
    Z.S. Altschuler, U.S. Geological Survey
Distribution of Nonphosphorus Constituents in Raw Materials Production
    James E. Lawver, International Minerals and Chemical Corporation
Chemical Processing Influence on Some Phosphate Ore Constituents
    K.L. Parks, Agrico Chemical Company
Distribution of Nonphosphatic Constituents (in Phosphate Rock) in Thermal Processing
    J.C. Barber, Consultant
Fate of Nonphosphorus Constituents of Phosphate Fertilizers Applied to Soils
    J.J. Mortvedt and P.M. Giordano, TVA National Fertilizer Development Center
Nutritional and Industrial Effects of Accessory Elements in Phosphate Rock
    J.R. Van Wazer, Vanderbilt University
Environmental Considerations of Nonphosphorus Constituents: Permits and Regulations
    R.S. Hearon, International Minerals and Chemicals Corporation
Biological Considerations Relevant to Minor Contaminants in Phosphate Ores
    J.J. Hefferren, American Dental Association Health Foundation
Current Government Research Activities on Accessory Elements in Phosphate
    C.H. Davis, Tennessee Valley Authority H.O. Poppleton, U.S. Bureau of Mines James Cathcart, U.S. Geological Survey
Current Research in Academic Institutions on Accessory Elements in Phosphates
    P. Somasundaran, Columbia University

Some speakers presented materials extemporaneously or from brief notes and slides; others presented information from informal papers.

WORKSHOP PARTICIPANTS

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REDISTRIBUTION OF ACCESSORY ELEMENTS AND COMPOUNDS FROM MINING AND PROCESSING OF NON-BAUXITIC ALUMINA ORES

SUMMARY

There has been renewed interest during the past several years in the recovery of aluminum from non-bauxitic ores, stimulated by the increasing cost of bauxite and refined alumina from traditional overseas sources. Though the cost of producing aluminum from non-bauxitic ores may be higher than from bauxite, lower shipping costs and the stability of the sources of supply may offset any cost disadvantage.

The United States is abundantly endowed with a variety of non-bauxitic aluminum resources. Those that are most suitable for the processing and recovery of cell-grade alumina are high-alumina clays, alunite deposits, dawsonite in oil shales, anorthosites, and nepheline syenites. The nature of the resource determines the process required to produce a refined alumina product, and the accessory materials that will be redistributed during the processing are determined by both the type of material to be processed and the process used. The content, possible problems, and byproduct possibilities of accessory elements associated with each resource are summarized below.

High-Alumina Clays

High-alumina clays consist predominantly of kaolinite and contain over 30 percent alumina. The principal U.S. source of kaolinite is in Georgia and South Carolina, where up to 9 billion tons of it may be found. Major impurities in these deposits are silica, iron oxide, and titania. Trace elements showing enrichment are gallium, chromium, vanadium, and thorium. Arkansas and Oregon contain smaller deposits of high-alumina clays, totalling about .4 billion tons each.

High-alumina clays would be mined by open-pit methods. Recovery processes that have been tested to the pilot plant stage and might be used on high-alumina clays are the hydrochloric acid process, nitric acid process, sulfurous acid process, sulfuric acid process, and the Pechiney H' sulfuric acid process.

Possible commercial byproducts from alumina production are silica, iron oxide, and titania. Vanadium and thorium appear to be the only trace metals that might cause environmental problems, but not enough is known about their fate during acid-extraction processes to make an adequate assessment at this time.

Alunite

Pure alunite, $KAl_3(OH)_6(SO_4)_2$, contains 37 percent alumina. It occurs as disseminated deposits, each consisting of a few million to more than a billion tons of alunite-bearing rock. The most promising deposits contain 25 to 50 percent alunite. It is estimated that the United States contains more than 2.5 billion tons of 30-percent alunite, most of it in the West.

Apart from potassium, there are no accessory elements of current economic importance in most alunite deposits. In general, the concentrations of minor and heavy elements in alunite are about equal to or lower than those in silicic-to-intermediate igneous rocks. An exception is where alunite is associated with metallic ores; such deposits may contain anomalous concentrations of Cu, Pb, Zn, and Mo, as well as Ag, Hg, As, B, and Ba.

It is expected that alunite deposits will be mined only by surface methods in the foreseeable future. Weathering of the wastes from alunite mining could result in oxidation and leaching of small amounts of pyrite, but it is unlikely that there will be significant environmental effects from this or other accessory constituents redistributed in the mining process.

There are two groups of methods of processing alunite:

1. caustic-leach methods (Alumet and Russian Processes), and
2. acid-leach methods (University of Guanajuato or UG Process, and the Kalunite Process).

All processes produce potassium sulfate as a coproduct. The Alumet and Russian processes also produce sulfuric acid. No problems are foreseen in disposing of tailings from alunite-processing plants.

Dawsonite in Oil Shale

Dawsonite [$NaAl(OH)_2CO_3$], nahcolite [$NaHCO_3$], and halite [NaCl] are associated with the oil shale in the Piceance Creek Basin of Colorado. The dawsonitic oil shale occupies an area of 500 square miles, ranges from a few feet to as much as 1,100 feet in thickness, and averages 10 percent dawsonite.

Dawsonitic oil shale is enriched in Mo, Pr, Cs, Ag, Sr, S, Cl, As, Sb, F, Si, Ta, and P by as much as 10 times the average abundance in sedimentary rocks, with molybdenum enrichment the greatest. Pyrite is thought to be the mineral host of many of the trace metals.

The most likely method of recovering alumina from dawsonitic oil shale would be the leaching of retorted oil shale with a mild caustic solution. Products of alumina recovery would include nahcolite and conventional products of oil shale, including hydrocarbons, elemental sulfur, and ammonia.

Disposal of the spent oil shale could involve problems of dust control, and leaching would be enhanced by the increased surface area. Unrecovered sulfides could oxidize to water-soluble sulfate, and sizable quantities of the carbonates of calcium, magnesium, and sodium, and of sodium chloride could be dissolved.

Most accessory constituents in explored oil shale deposits are in concentrations too low to be economic, and their lateral distributions are not known. Significant enrichment of uranium, tin, and arsenic in the waters and oils obtained from retorting could occur. Uranium is of particular interest. Some noxious elements, especially boron, fluorine, and arsenic, could be mobilized during retorting or by leaching of the spent shale.

Much further study is needed of the accessory constituents in oil shale and their redistribution during processing.

Anorthosite and Nepheline Syenite

Anorthosite and nepheline syenite are igneous rocks containing above-average concentrations of alumina (30 percent and 20 percent, respectively). Both of these rocks, because of their alkaline nature, can be processed to recover alumina by either the lime-soda-sinter or lime-sinter-soda leach processes. The former has been tested successfully by the U.S. Bureau of Mines to the pilot-plant stage using anorthosite feed.

Anorthosite consists principally of plagioclase together with less than 10 percent of clinopyroxene and orthopyroxene. Deposits range in size from very large intrusions covering more than 1,000 square miles to small pods or stringers. Many billions of tons are available in the United States in exposed or near-surface deposits.

Few accessory elements are present in anorthosite at concentrations greater than the average for the earth's crust, and none has any economic or environmental significance. Possible byproducts of alumina recovery from anorthosite include potash, soda ash, and cement.

Nepheline syenite is a coarsely crystalline igneous rock composed of alkali feldspars and nepheline. It occurs mostly as small stocks or ring complexes averaging 3 miles in diameter. It is broadly distributed in the Appalachian and Ouachita Mountains and in the western United States.

There are few references to accessory element concentrations in nepheline syenites in the United States. There is evidence that the elements As, Ba, Ce, La, Mo, Nb, Pb, Sr, and V may be present in concentrations 5 to 10 times the average crustal abundance, but only Ce, La, and Nb have possible economic significance. Possible byproducts of alumina recovery include potash, soda ash, and cement.

It is not certain whether the mining and processing of either anorthosite or nepheline syenite would lead to any significant environmental problems since there is too little information on which to base an estimate.

INTRODUCTION

During the past few years, interest in the recovery of aluminum from domestic non-bauxitic ores has been renewed because of the increasing cost of imported bauxite and aluminum. Some bauxite-producing countries have nationalized their industries, others have increased taxes and royalties on mined bauxite or refined aluminum, and the political climate in some is such that interruption of supply is possible. Furthermore, efforts are being made to control prices through a cartel organization. Aluminum is a critical material industrially and militarily. It is clearly important, therefore, that we have alternative domestic sources of supply.

Although alumina (Al_2O_3)is ubiquitous, constituting no less than 15 percent of the earth's crust, it is expensive to separate and purify into a form suitable for production of aluminum. An exception is the alumina contained in bauxite, the end-product of the natural weathering of iron-poor rocks in tropical climates. Bauxite contains 45 percent or more of Al_2O_3. No other readily processable source with a higher concentration of aluminum exists in great quantities.

The United States is abundantly endowed with a variety of non-bauxitic aluminum resources that could substitute for bauxite. The Alumina Panel has concentrated its study on those resources it believes to be the most suitable for processing and recovery of cell-grade alumina. Cell-grade alumina is refined alumina that meets stringent specifications for purity and uniformity with respect to accessory element concentration, particle-size distribution, and calcination level; only very narrow ranges of variation are permissible for proper function of the reduction cells in producing aluminum from alumina. The most suitable resources are: (1) high-alumina clays; (2) alunite deposits; (3) dawsonite in oil shales; (4) anorthosites; and (5) nepheline syenites.

Individual deposits may not necessarily be developed in this order since economic factors will strongly influence the timing and nature of development. Moreover, the opportunity to produce coproducts, such as sodium bicarbonate from Colorado oil shale, would probably improve the chances of aluminum production from a particular source. Other potential aluminum sources, such as saprolite, kyanite, and fly ash, appear unlikely to be exploited for aluminum because they contain lower concentrations or would be more difficult to process than those considered in this study.

Aluminum is recovered by electrolysis in Hall cells from a melt composed of purified (cell-grade) alumina and cryolite. The cell-grade alumina feedstock is commonly obtained by treating bauxite, using the Bayer process. This process is normally suitable only for bauxitic ores containing less than 10 percent silica. Ores containing larger amounts of silica, or other constituents in substantial amounts, require different treatment depending on the nature and type of ore. However, the product from all such processes must be a purified form of alumina suitable for electrolysis, because no other process than electrolytic recovery using Hall cells has proved to be commercially feasible.

The process required to produce a cell-grade alumina from other than bauxitic ores depends largely on the nature of the resource. Recent unpublished studies by the U.S. Bureau of Mines have shown that most processes for treating non-bauxitic aluminum ores require between 2.4 and 3.2 times the energy of the traditional Bayer process. The energy penalty and the greater complexity of these processes would increase the cost of aluminum by amounts ranging from nearly 1¢ to as much as 5¢ per pound. Under favorable circumstances, this greater cost would be partly offset by a reduction in the cost of mining and shipping the ore and by the exploitation of accessory constituents as coproducts.

Each of the five sections of this report reviews the behavior of accessory elements during the mining and processing of one of the alumina resources listed above. Information is also given on the estimated tonnage and distribution of each type of resource.

In our study of these resources, no significant environmental hazards associated with accessory constituents related to aluminum production have been identified. However, little is known either of the trace-element content or the behavior of trace elements during processing for the production of cell-grade alumina. Attempts are made to compare the apparent trace-element concentrations in the alumina resources discussed with the average abundance of these elements in the earth's crust, in an effort to identify those elements that may warrant further attention. In the absence of other criteria, this approach is useful in focusing on relevant problem areas, but caution is needed in drawing conclusions without taking into account other considerations.

Attention should be given to the possible leaching of fluorine and arsenic from dawsonitic oil shale residues, and to the possibility of pyrite oxidation in some alunite waste. Both anorthosite and nepheline syenite waste may leach and produce alkaline runoff. These problems are considered minor on the basis of available information, but they should be investigated on a case-by-case basis if exploitation of a deposit proves likely.

Potential byproducts include silica from clays, potash and sulfuric acid from alunite, soda ash from dawsonite, and soda ash and potash from anorthosite and nepheline syenite. Other minor constituents might be recovered, but assessment of their recoverability must wait for more detailed technologic studies than are currently available.

HIGH-ALUMINA CLAYS

The term kaolin is used both as a rock term and as the name of a group of clay minerals that include kaolinite, dickite, nacrite, and halloysite (Ross and Kerr 1931). Kaolin is processed by both wet and dry methods (Murray 1963a) for use as a filler and pigment in the paper, and for use in paint, plastics, rubber, ink, catalyst, ceramic and many other industries (Murray 1963b).

The mineral kaolinite contains 39 percent Al_2O_3 and is therefore regarded as a potential source of aluminum. Many deposits of kaolin are relatively pure and contain more than 30 percent alumina; bauxitic kaolins may contain as much as 45 percent alumina.

Georgia-South Carolina Kaolin Belt

The Georgia-South Carolina kaolin belt (Figure 5.1) extends southwest-northeast across Georgia from Columbus to Augusta and northeastward about 90 miles into South Carolina. The center of the kaolin industry is in South Carolina at the town of Aiken.

The kaolin deposits occur as irregular, elongate, lenticular sedimentary bodies in thick sand units of late Cretaceous and early Tertiary age. The deposits average between 15 and 30 feet in thickness and may be as much as 60 feet thick. Individual deposits extend laterally for distances ranging from a few tens of feet to several miles, and 80 percent or more of their total volume consists of the mineral kaolinite. There are perhaps 8.5 to 9 billion tons of kaolin in the Georgia-South Carolina belt. Approximately 5 million tons of kaolin from this area were sold in 1976.

Chemical analyses of kaolin vary; Table 5.1 lists typical concentrations and general ranges. Trace elements that occur in enriched concentrations in these kaolins are Ga, Cr, V, and Th.

All present mining is in open pits. The overburden ranges from 25 to 150 feet in thickness and consists of red sands, white sands, fuller's earth (calcium bentonite), and sandy clays. The sands are aquifers, and water can present a serious problem to mining in certain areas at the southeastern edge of the belt. The beds dip 1 to 2 degrees per mile southeastward toward the Atlantic Ocean from the contact of the coastal plain sedimentary rocks with the crystalline rocks of the Piedmont. If kaolin becomes an economic source of alumina, the Georgia-

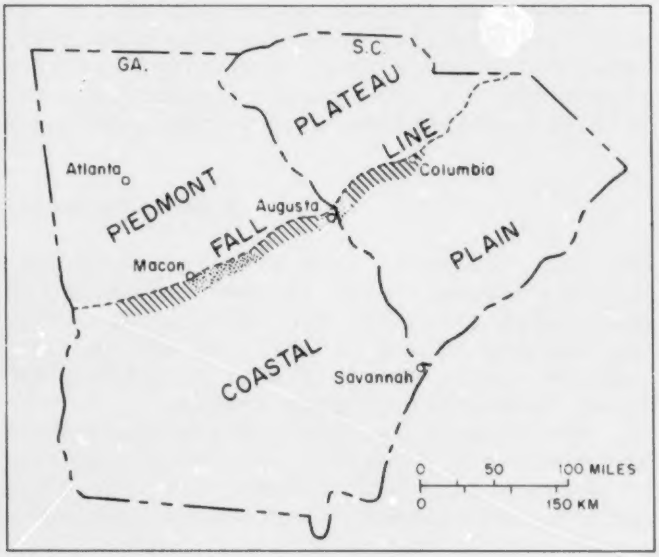


FIGURE 5.1 Georgia-South Carolina kaolin belt.

SOURCE: Murray (1976).

TABLE 5.1 Chemical Analysis of Kaolin

	Weight percent		
	Typical	Low	High
SiO_2	44.0	50.2	40.6
Al_2O_3	38.5	31.5	44.4
Fe_2O_3	0.45	1.21	0.94
TiO_2	1.10	1.82	1.42
K_2O	0.18	0.24	0.24
H_2O	15.77	16.03	12.40

SOURCE: Hinckley (1961).

South Carolina kaolin belt will be the primary kaolin-mining area in the United States.

Other Areas

Other areas of kaolin deposits in the United States are shown on Figure 5.2. All contain very much smaller potential tonnages of kaolin than the Georgia-South Carolina belt and have lower aluminum content, as summarized in Table 5.2.

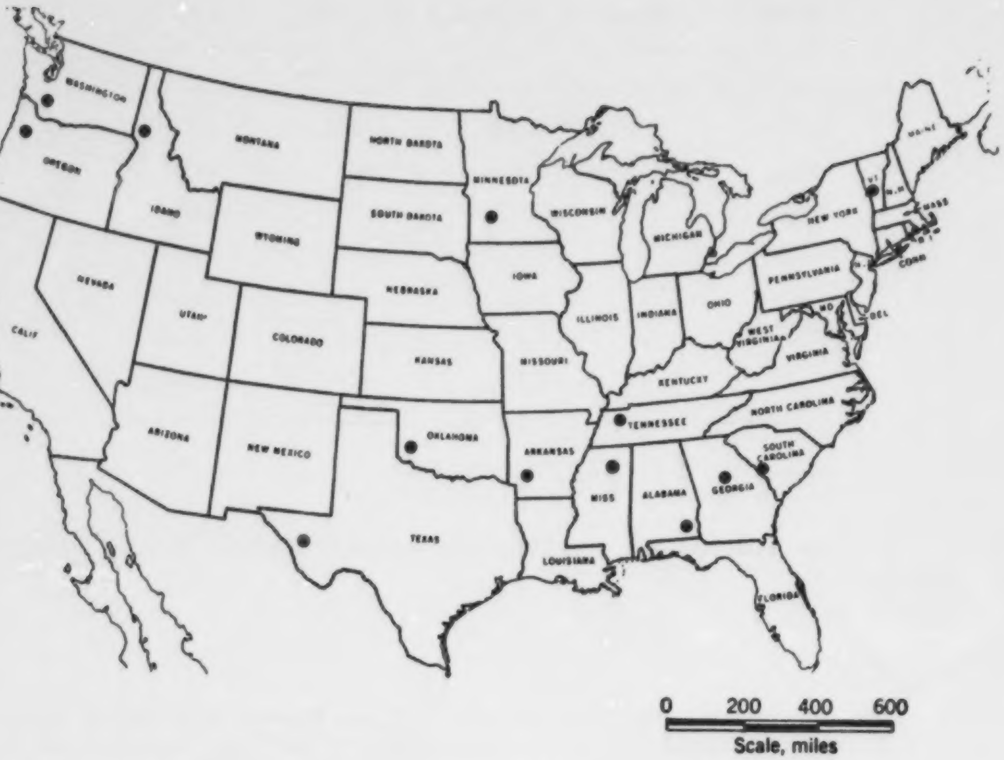
Only the Arkansas and Oregon deposits can be considered potential producers of kaolin in the foreseeable future. The kaolins in Arkansas are associated with bauxites, and some of the bauxitic kaolins are now being mined as sources of alumina. The Oregon kaolins are associated with bauxites and laterites and are relatively thick.

Fireclays are associated with coal seams of Pennsylvanian age in several eastern and midwestern states, California, and Montana (Figure 5.3). The U.S. Bureau of Mines (1967) estimates that these states contain over 8 billion tons of fireclay with an average of 27 percent Al_2O_3. Because these fireclays could be mined along with the overlying coal, they should be considered potential sources of alumina. Ohio contains the largest of the U.S. fireclay resources, with more than 4 billion tons.

Accessory Elements in High-Alumina Clays

The major accessory constituent in the kaolins of Georgia and South Carolina is silica, and there are minor amounts of the elements Fe, Ti, Mg, Ca, Na and K. Table 5.3 shows analyses of South Carolina and Georgia kaolins (Weaver and Pollard 1973).

Hinckley (1961) analyzed several kaolin samples from Georgia and South Carolina for B, Ga, and Mn, and the American Petroleum Institute Reference Clay Mineral Study (Kerr et al. 1949) gives chemical and


WASHINGTON
OREGON
IDAHO
MONTANA
NORTH DAKOTA
SOUTH DAKOTA
WYOMING
MINNESOTA
WISCONSIN
MICHIGAN
NEW YORK
MAINE
VT
N.H.
MASS
CONN
PENNSYLVANIA
NEVADA
UTAH
COLORADO
NEBRASKA
IOWA
ILLINOIS
INDIANA
OHIO
WEST VIRGINIA
VIRGINIA
MD
DEL
CALIF
KANSAS
MISSOURI
KENTUCKY
TENNESSEE
NORTH CAROLINA
SOUTH CAROLINA
ARIZONA
NEW MEXICO
OKLAHOMA
ARKANSAS
MISS
ALABAMA
GEORGIA
TEXAS
LOUISIANA
FLORIDA
0
200
400
600
Scale, miles

SOURCE: Murray and Patterson (1975).

FIGURE 5.2 Kaolin deposits in the United States.

trace-element analyses of one South Carolina and two Georgia kaolins. Trace elements detected in measurable quantity in these analyses were Ba, B, Cr, Cu, Ga, Pb, Mn, Ni, Sr, V, and Zn.

Silica is also the major accessory constituent in the Arkansas and Oregon kaolins. Trace-element analyses are not available.

The fireclays are more variable in their chemistry than the kaolins, and again silica is the major accessory constituent (O'Neill et al. 1965). Trace-element analyses (Keller 1968) indicate that Ba, V, Zr, Mn, Cu, Ni, Zn, Ga, Cr, and B are present in detectable quantities. Table 5.4 gives analyses of fireclays from Pennsylvania and flint clays from Missouri and Pennsylvania.

Recovery Processes and Related Redistribution of Accessory Constituents

High-alumina clays have been evaluated as a source of aluminum in several foreign countries as well as in the United States. There is, however, no known commercial plant anywhere in the world. Large-scale, pilot-plant testing is being done by Pechiney in France, and various tests have been made by the U.S. Bureau of Mines.

The most likely first step in a commercial alumina-from-clay process is the strip mining of kaolin. This would not in itself lead to mobilization of accessory constituents. It is probable, however, that the residue from acid extraction, consisting largely of silica and some heavy-metal oxides, would be returned to the mine site. The difficulties and problems in strip mining of kaolin would be those that are typical of most strip mining (Ward and Husted 1976).

Depending on the acid chosen as solvent, the kaolin might or might not be calcined prior to extraction. Calcination presents a potential but controllable air pollution problem.

The next step, extraction with acid, dissolves the alumina, significant amounts of iron oxide, and some of the oxides present in minor or trace amounts, principally those of Ti, Na, K, Ga, Cr, V, and Th. Most of the silica is rejected, and is separated from the liquor by filtration. In most acid processes, iron is removed from the leachate in a distinct step (for example, by solvent extraction) as a salt, which is then hydrolyzed to ferric oxide and disposed of in impoundments.

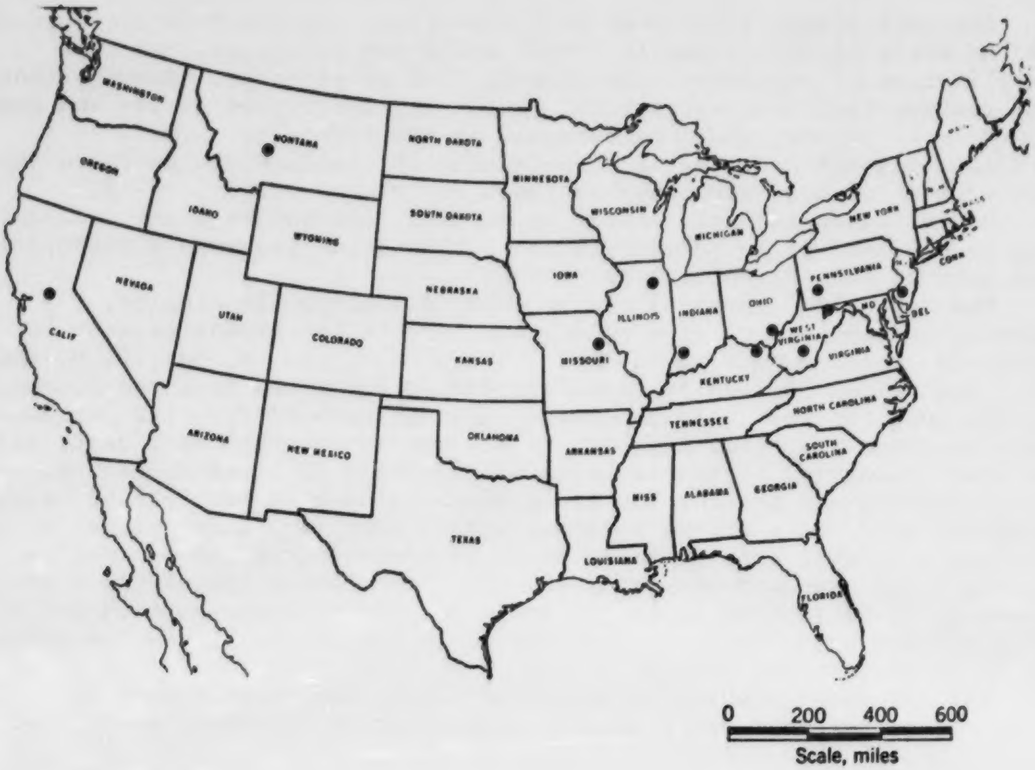
Pigment-grade kaolins for the process industries are leached using sulfuric acid and a strong reducing agent, such as sodium hydrosulfite, to form a soluble iron sulfate, which is removed from the process in the filtrate and disposed of by impoundment. The kaolin industry's current practice is to impound an acidic solid residue that has settled out and to treat the clear water so that the pH is nearly neutral as the water is released into the streams.

The dissolved alumina is separated from other constituents by crystallization as a salt, which is subsequently calcined to alumina,

TABLE 5.2 Estimated Kaolin Tonnage and Grade in States Other than Georgia and South Carolina

	Millions of tons, estimated	Average Al_2O_3 content, percent
Alabama	120	33
Arkansas	545	31
Idaho	120	25
Minnesota	127	33
Mississippi	30	33
Oklahoma	300	25
Oregon	518	28
Tennessee	30	32
Texas	212	33
Vermont	31	29
Washington	80	31

SOURCE: U.S. Bureau of Mines (1967).


WASHINGTON
OREGON
CALIF
IDAHO
NEVADA
MONTANA
WYOMING
UTAH
ARIZONA
COLORADO
NEW MEXICO
NORTH DAKOTA
SOUTH DAKOTA
NEBRASKA
KANSAS
OKLAHOMA
TEXAS
MINNESOTA
IOWA
MISSOURI
ARKANSAS
LOUISIANA
WISCONSIN
ILLINOIS
MICHIGAN
INDIANA
OHIO
KENTUCKY
TENNESSEE
MISS
ALABAMA
GEORGIA
FLORIDA
SOUTH CAROLINA
NORTH CAROLINA
VIRGINIA
WEST VIRGINIA
PENNSYLVANIA
NEW YORK
MD
DEL
CONN
0
200
400
600
Scale, miles

SOURCE: Murray and Patterson (1975).

FIGURE 5.3 Fire clay resources in the United States.

with recovery of the associated acid (National Research Council 1970). The level of impurities in the leachate is controlled by removal of a small bleed stream, which is disposed of by evaporation followed by impoundment of the solid residue. Thus, current practice in the mining and processing of kaolin to produce sodium silica aluminate does not appear to mobilize any hazardous accessory materials.

There remain the possible environmental hazards introduced by reagents, which will vary with the process chosen.

The following are the major probable recovery processes: (a) hydrochloric acid process; (b) nitric acid process; (c) sulfurous acid process; (d) sulfuric acid process; and (e) Pechiney "H⁺" sulfuric acid process.

Acid processes are considered the most promising for alumina production from clays.

Hydrochloric Acid Process

Extraction of alumina from clay by hydrochloric acid has been demonstrated (Barclay and Peters 1976), and generalized flowsheets have been published (Figure 5.4). Spectrographic and quantitative determinations have been made for both feed material and wastes. (For proprietary reasons, details of process variations are not yet available.)

Raw clay and hydrochloric acid are the primary feed materials. In-process solution additives include a tertiary amine-deconol-kerosene mixture. The composition of the raw clay, by weight, is approximately 95 percent $Al_2O_3/SiO_2/H_2O$. Iron and titanium comprise the balance, along with a host of minor elements. Solid products either remain in the tailings or are decomposed. In turn, decomposition produces Fe_2O_3 and reduction-grade Al_2O_3. The tailings are approximately 94 percent by weight SiO_2 and H_2O. Unrecovered Al_2O_3, along with TiO_2 and minor quantities of other oxides and chlorides, make up the balance.

The major accessory constitutents associated with the use of the hydrochloric acid process on Georgia clays are SiO_2, Fe_2O_3, and TiO_2. A 400-ton-per-day (TPD) alumina plant generates more than 700 TPD of residue, which is approximately 90 percent by weight SiO_2. The small tonnage of high-purity iron oxide that is produced has questionable marketability. Economically feasible recovery methods for titanium have

TABLE 5.3 Accessory Constituents in South Carolina and Georgia Kaolins (weight percent)

Major Constituents	Bath, South Carolina	Dry Branch, Georgia
SiO_2	43.60	42.81
Al_2O_3	37.91	37.67
H_2O^+	13.62	13.29
Total	95.13	93.77
Minor Constituents		
Fe_2O_3	0.25	0.86
TiO_2	1.96	2.32
MgO	0.05	0.20
Other Constituents	1.89	1.83
SiO_2/Al_2O_3	1.95	1.93
$SiO_2/(Al_2O_3 + Fe_2O_3)$	1.94	1.91

SOURCE: Weaver and Pollard (1973), courtesy of Elsevier Scientific Publishing Co., Geo-Sciences Department, Amsterdam.

not been developed. The accessory elements associated with this process are not considered significant as possible byproducts. The wastes that are generated (silica, iron oxide, and titania) are considered nonhazardous and can be disposed of by conventional techniques. At present, in the manufacture of sodium silica aluminate, all are impounded with no deleterious environmental results.

Strip mining of the relatively shallow clays would provide disposal sites for wastes that could be recontoured and reclaimed as mining progresses. Federal and state standards and regulations require a commitment to environmental quality before any plant can be granted a permit. Liquid, solid, and gaseous wastes are controllable by known techniques.

Nitric Acid Process

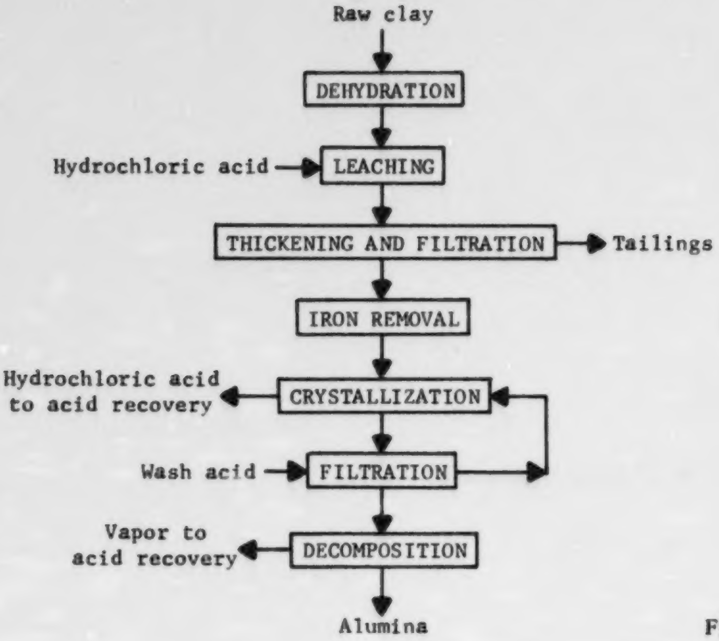
Although the energy consumption and extraction efficiencies of the nitric acid and the hydrochloric acid extraction processes are different, their potential byproducts and waste effluents are

TABLE 5.4 Analyses of Fireclays from Pennsylvania and Flintclays from Pennsylvania and Missouri (percent)

	Fireclay from Armstrong Co., Pa.	Fireclay from Clearfield Co., Pa.	Flintclay from Clearfield Co., Pa.	Flintclay from Missouri
SiO_2	70.30	55.15	40.70	42.68
Al_2O_3	17.50	28.70	40.57	38.49
Fe_2O_3	1.17	1.06	0.53	1.55
FeO	0.91	0.80	0.72	
CaO	0.09	0.15	0.16	
MgO	0.37	0.46	0.19	0.08
K_2O	1.27	2.20	1.35	0.49
Na_2O	0.39	0.40	0.60	0.28
TiO_2	1.50	1.67	2.57	2.90
LOI*	6.45	9.36	12.59	
S	0.20	0.07	0.03	
CO_2	0.53	1.57	1.14	
Comb H_2O	5.06	7.16	11.15	14.07
H_2O @ 120°C	0.66	0.63	0.30	

*Loss on ignition.

SOURCE: Pennsylvania analyses from O'Neill (1965); Missouri analyses from Keller (1968).


Raw clay
DEHYDRATION
Hydrochloric acid
LEACHING
THICKENING AND FILTRATION
Tailings
IRON REMOVAL
Hydrochloric acid to acid recovery
CRYSTALLIZATION
Wash acid
FILTRATION
Vapor to acid recovery
DECOMPOSITION
Alumina

SOURCE: Barclay and Peters (1976).

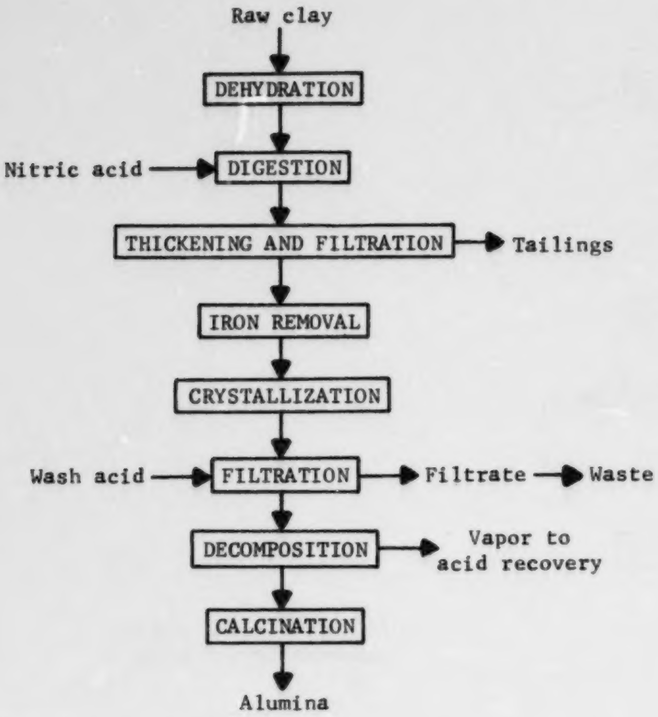
FIGURE 5.4 Block plan for processing clay with hydrochloric acid.

essentially the same. During thermal decomposition, however, oxides of nitrogen are formed that must be converted to nitric acid. Stack losses can occur at decomposition, waste nitrate recovery, and acid recovery (Peters et al. 1964), as indicated in Figure 5.5. Quantification of all effluents will be required for issuance of operating permits.

Sulfurous Acid Process

In this process (Peters et al. 1962), calcined clay is fed into digesters containing a solution of about 20 percent H_2SO_3 at 55°C and an SO_2 pressure of 9 atmospheres (Figure 5.6). After extraction of alumina and relief of pressure, silica is removed by filtration. The filtrate and washings are autoclaved at 100°C and an SO_2 pressure of 3 atmospheres to precipitate a monobasic sulfite, $Al_2O_3-2SO_2-5H_2O$, which is then autoclaved at 155°C and a steam pressure of 7 atmospheres to reject SO_2 and produce a crude $Al_2O_3-2H_2O$ as a feed to a modified Bayer process.

The sulfur dioxide evolved from the second hydrolysis step must be recaptured (well-known techniques are available) and not allowed to escape into the atmosphere.


Raw clay
DEHYDRATION
Nitric acid
DIGESTION
THICKENING AND FILTRATION
Tailings
IRON REMOVAL
CRYSTALLIZATION
Wash acid
FILTRATION
Filtrate
Waste
DECOMPOSITION
Vapor to acid recovery
CALCINATION
Alumina

SOURCE: Barclay and Peters (1976).

FIGURE 5.5 Block plan for processing clay with nitric acid.

Sulfuric Acid Process

As described by Peters et al. (1963), in this method calcined clay is fed into a solution of about 40 percent sulfuric acid at atmospheric pressure (Figure 5.7). The undissolved silica is removed by filtration. Then iron is removed from the leachate, either by precipitation as ferric manganese sulfate upon addition of manganese sulfate and ozone, or by electrolysis. In neither method would there be novel disposal problems. As with other processes discussed above, silica, iron, and acidic wastes can be handled as are the industrial wastes of many process industries, with no serious disposal problems.

The iron-free solution of aluminum sulfate is concentrated by evaporation, and the resulting crystals of hydrated $Al_2(SO_4)_3$ are hydrolyzed to alumina. The mixture of SO_2 and SO_3 that is evolved must be converted to sulfuric acid, and any associated environmental problems would be similar to those of existing sulfuric acid plants.

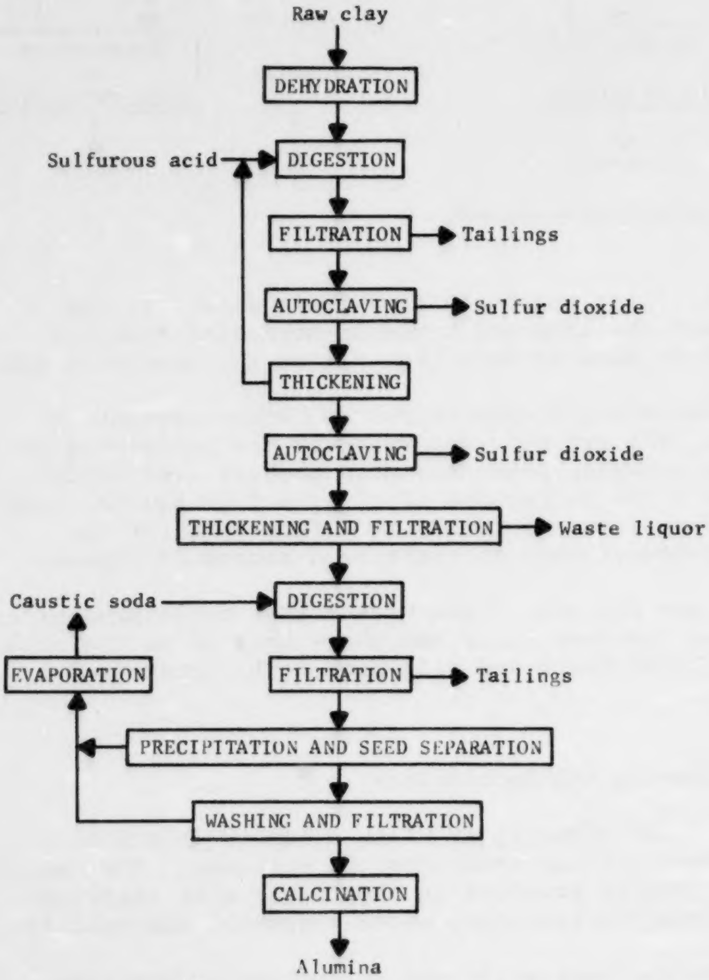
Pechiney "H+" Sulfuric Acid Process

In this process, as described by Cohen and Margier (1976), calcined or raw ore is leached with sulfuric acid (Figure 5.8). Silica removal and crystallization of aluminum sulfate are similar to those steps in the sulfuric acid process. The aluminum sulfate is not hydrolyzed, however, but is converted to aluminum chloride, which is crystallized and converted to alumina in the same way as in the hydrochloric acid process.

The problems of SO_2 and SO_3 recovery are the same as in the sulfuric acid process, as is the recovery of HCl as well.

Byproducts

Silica, iron oxides, and titania are the major byproducts that would result from acid-extraction processes to produce alumina from high-alumina clays. The tonnage of silica residue would exceed that of the recovered alumina by 10 to 20 percent. This residue retains essentially the same crystal shape as the kaolin (pseudo-hexagonal) and has a very


Raw clay
DEHYDRATION
Sulfurous acid
DIGESTION
FILTRATION
Tailings
AUTOCLAVING
Sulfur dioxide
THICKENING
AUTOCLAVING
Sulfur dioxide
THICKENING AND FILTRATION
Waste liquor
Caustic soda
DIGESTION
EVAPORATION
FILTRATION
Tailings
PRECIPITATION AND SEED SEPARATION
WASHING AND FILTRATION
CALCINATION
Alumina

SOURCE: Barclay and Peters (1976).

FIGURE 5.6 Block plan for processing clay with sulfurous acid.

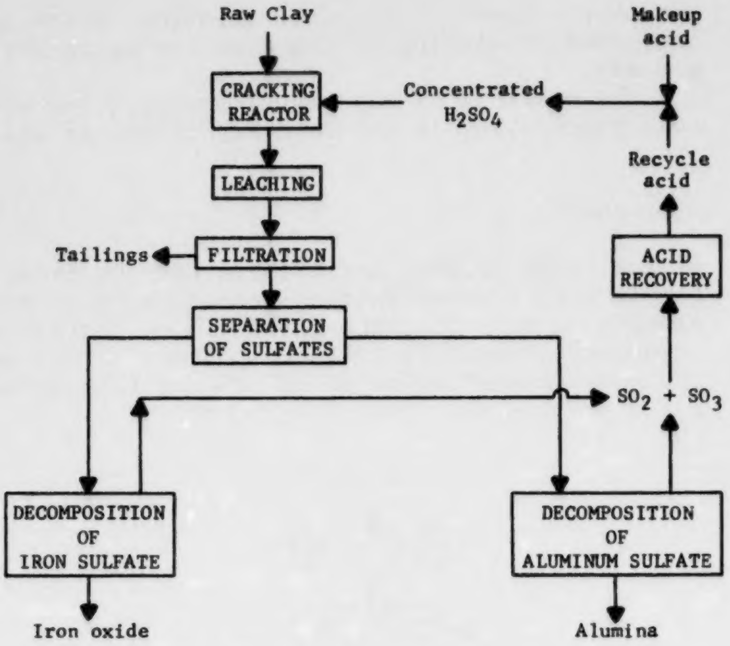

Raw Clay
Makeup acid
CRACKING REACTOR
Concentrated H_2SO_4
Recycle acid
LEACHING
Tailings
FILTRATION
ACID RECOVERY
SEPARATION OF SULFATES
$SO_2 + SO_3$
DECOMPOSITION OF IRON SULFATE
DECOMPOSITION OF ALUMINUM SULFATE
Iron oxide
Alumina

FIGURE 5.7 Block plan for processing shales with sulfuric acid.

SOURCE: Barclay and Peters (1976).

high surface area because of its extremely fine grain size. If the color could be improved and the iron and titanium separated from the silica, this byproduct would make an excellent filler for newsprint and rubber.

Iron-oxide recovery would not be economical and would present no serious disposal problem. The red muds generated in the production of alumina from bauxite, for example, present a much greater iron-oxide disposal problem than would the extraction of alumina from kaolin. The titania content of the clays ranges from 1.5 to 2.5 percent; if the titania sludge could be concentrated, it might be a source of pigment-grade TiO_2.

Vanadium and thorium are the only trace metals that could present an environmental problem, but how they occur and where they go in the acid-extraction processes is little known and will have to be determined by future testing.

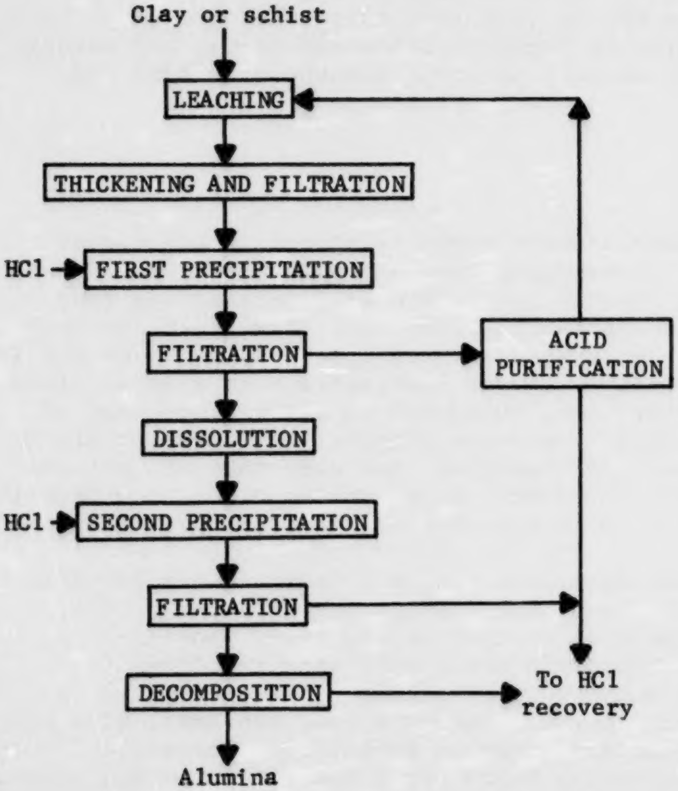
Summary and Conclusions

The mining of the clay and the disposal of waste products from acid processes should not present serious environmental problems. The kaolin industry is now handling similar problems in compliance with state and federal guidelines for mining reclamation, waste disposal, air quality, and water quality.

With regard to processing, more pilot and production information must be gathered before we can know whether there would be serious environmental problems. Trace constituents do not appear to present problems, but the fate of thorium and vanadium during acid-extraction processing should be determined.

Acid processes for extracting alumina from clays have been tested in pilot plants. The clays studied were chosen on the basis of recoverable Al_2O_3. Processing residues have not been specifically identified as useful byproducts or as waste materials. The major residue is SiO_2; there are only minor amounts of accessory elements, and it is not anticipated that there will be any major redistribution of these. Both the HCL and HNO_3 processes can be designed and operated to meet current environmental requirements.

Pilot-plant evaluations now being carried out by the Bureau of Mines at Boulder City, Nevada, will provide additional detailed information from which projections can be made. The Desert Research Institute, University of Nevada, has been awarded a contract to develop and test an environmental monitoring program that will be applicable to the operation of any alumina-extraction system.


Clay or schist
LEACHING
THICKENING AND FILTRATION
HCl
FIRST PRECIPITATION
FILTRATION
ACID PURIFICATION
DISSOLUTION
HCl
SECOND PRECIPITATION
FILTRATION
DECOMPOSITION
To HCl recovery
Alumina

SOURCE: Barclay and Peters (1976).

FIGURE 5.8 Block plan for the Pechiney H+ process.

ALUNITE

Alunite is a complex aluminum-bearing mineral, which in the pure form, $KAl_3(OH)_6(SO_4)_2$, contains about 37 percent alumina. Sodium may substitute for potassium in the crystal lattice, and when the sodium content exceeds that of potassium the mineral is called natroalunite. Alunites occur as coarsely crystalline aggregates and as dense earthy masses resembling clay minerals in appearance.

Alunite occurs in sedimentary, metamorphic, and igneous rocks; it occurs as vein and bedded sedimentary deposits of virtually the pure mineral and as disseminated aggregates in igneous rocks. The vein and bedded deposits of alunite rarely exceed a million tons in size, and it therefore appears unlikely that they will be sources of alumina within the foreseeable future.

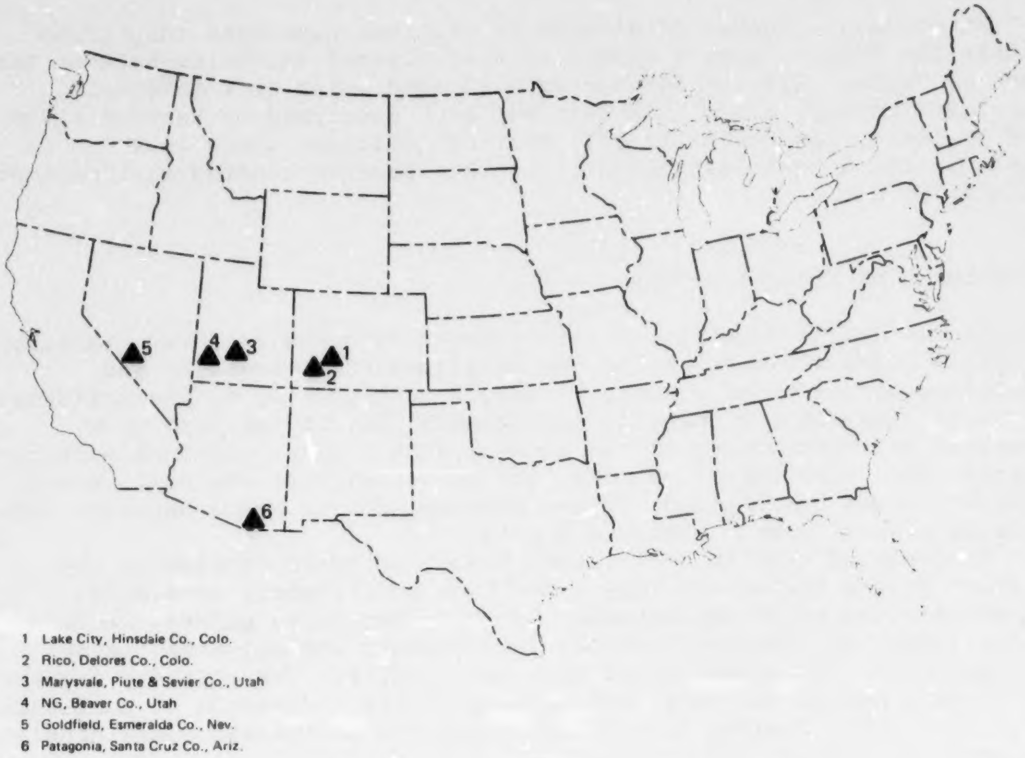
Resources

Deposits of alunite disseminated in hydrothermally altered volcanic and subvolcanic igneous rocks have been identified that are estimated to contain from a few million to more than a billion tons of alunite-bearing rock per deposit. Deposits containing 25 to 50 percent alunite appear to be the most promising sources for the production of alumina on a commercial scale. The alunite resources of the United States are estimated to be no less than 2.5 billion tons of rock containing 30 percent or more alunite, and may be more than twice that amount. The bulk of these resources is in the deposits discussed below, but several dozen additional deposits (generally of lower tonnage or grade) are known.

Location of Deposits

Most of the large disseminated alunite deposits of the United States occur in altered acidic to intermediate Tertiary volcanic rocks in the western part of the country (Figure 5.9). The best defined are four large alunite deposits located about 30 miles west of Milford, Beaver County, Utah, in the Wah Wah Mountains. These deposits, known as the NG deposits, occur in hydrothermally altered intermediate to silicic flows and ignimbrites of mid-Tertiary age. Deposits of 120 million tons of alunite-bearing rock containing 38 percent alunite (14.2 percent Al_2O_3) have been classified as "measured" reserves, and more than 600 million tons of similar grade ore are inferred. Five smaller deposits within 15 miles of the NG deposits have estimated reserves of 20 to 100 million tons each.

The alunite deposits best described in the literature are found in the area around Marysvale, Piute County, and in Sevier County, Utah, about 75 miles east of the NG area (Butler et al. 1920, Thoenen 1941, and Callahan 1973). In the Marysvale area, more than two dozen disseminated alunite deposits of .5 to 10 million tons each occur in altered intermediate volcanic rock of Oligocene age; the small size of these deposits may limit their exploitation potential. Marysvale deposits were worked briefly during World War I for potassium and during


5
4
3
1
2
6
1 Lake City, Hinsdale Co., Colo.
2 Rico, Delores Co., Colo.
3 Marysvale, Piute & Sevier Co., Utah
4 NG, Beaver Co., Utah
5 Goldfield, Esmeralda Co., Nev.
6 Patagonia, Santa Cruz Co., Ariz.

SOURCE: NRC (1977).

FIGURE 5.9 Alunite deposits in the western United States.

World War II for alumina (Thoenen 1941, Fleischer 1944, and Callahan 1973).

Several alunite deposits in Colorado have been noted in the literature (Larsen 1913, and Thoenen 1941). The largest of these appears to be at Red Mountain near Lake City, Hinsdale County. This deposit, in altered latitic subvolcanic and intrusive rock, contains at least several hundred million tons of 36 to 40 percent alunite, and the total tonnage could exceed a billion tons (C.W. Bauer 1976, unpublished data, Earth Sciences, Incorporated, Golden, Colorado). An alunite deposit near Rico, Dolores County, was estimated by Thoenen (1941) to contain 6 million tons of 17 percent alunite. Recent more extensive mapping and sampling (Serna-Isaza, 1973, unpublished M.S. Thesis, Colorado School of Mines) suggest that the deposit contains 100 million tons of 20 percent alunite. The deposit occurs in a quartz monzonite stock intruding sedimentary rocks of Pennsylvanian age.

On Red Mountain, near Patagonia, Santa Cruz County, Arizona, altered rhyolitic and latitic volcanic rocks contain about 30 percent alunite. Shallow drilling suggests at least 300 million tons of alunite-bearing rock, and the actual tonnage may be much greater. Several smaller alunite deposits have also been identified in the surrounding area (Simons 1974; Corn 1975; and Bauer, unpublished data, Earth Sciences, Incorporated, 1975).

In Nevada, a number of alunite occurrences have been identified within the Walker Lane, a linear belt of altered volcanics between Reno and Las Vegas. Alunite associated with gold veins near Goldfield, Esmeralda County, along this belt has been described by Ransome (1909) and by Ashley and Keith (1973). West of Goldfield there is a disseminated deposit estimated to contain several hundred million tons of alunite ore.

Uniformity of Mineralization

Alunite mineralization varies from erratic to quite uniform. Variations within a deposit affect mining and metallurgical processing and therefore are of major concern. Factors contributing to the uniformity of mineralization are porosity and permeability of the host rock, strength and consistency of the mineralizing fluids, original host-rock composition, structural controls, and preparation of the host rock by fracturing and brecciation. These controls differ among deposits and, in some places, within a single deposit.

Hundreds of alunite occurrences have been noted throughout the western United States but only a few have sufficiently consistent mineralization to be exploitable. In many deposits, quartz, kaolin-group minerals, amorphous silica, iron oxides, and cristobalite or tridymite are intimately mixed with the alunite. The relative amounts of these minerals can vary dramatically within a distance of as little as 1 foot. The alunite deposit preferred for processing would consist entirely of alunite and quartz.

The NG deposits near Milford, Utah, are a fairly uniform quartz-alunite mixture and amenable to large-scale open-pit mining (Walker and Stevens 1974; and Perry, unpublished data, Earth Sciences, Incorporated, 1974). Information from drilling into several of the Marysvale, Utah, deposits in the mid-1940s suggests that they are not uniform in mineralization, which could complicate mining and metallurgical processing. Limited drilling and sampling at Lake City, Colorado, suggests that this alunite deposit is quite uniform. Drilling of the other deposits mentioned above has been insufficient to test the mineralogical consistency of the ore.

Deposit Geometry

The size and configuration of alunite deposits vary widely; they are affected by the same factors that control the uniformity of mineral distribution in the ore. The NG deposits near Milford, Utah, are mostly elongate and show evidence of strong structural control. Parts of the deposits are predominantly tabular in form, probably a result of porosity and permeability controls within favorable host volcanic units. The Lake City and Rico, Colorado, deposits are essentially circular and appear to be closely associated with volcanic necks or vents. A number of alunite deposits appear to be restricted to a single volcanic flow or unit. They are usually tabular and may be quite elongate.

In many places, altered minerals are distributed zonally around alunite deposits. Many show evidence of a hot-spring environment, with its typical horizontal zonation, i.e., a central core of massive silica or silicious sinter surrounded by an envelope of alunite-quartz that grades into an argillic halo (kaolinite, in these deposits), then into unaltered rock. Soviet scientists have noted a similar, but vertical, zonation in alunite deposits (Sidorenko 1970). Dimensions of these zones can vary greatly.

Development of Alunite Deposits

The NG alunite deposits in Beaver County, Utah, have been drilled for development, mine plans have been prepared, environmental studies have been completed, and a final Environmental Impact Statement was issued in August 1977. The metallurgical process has been tested in a pilot plant at Golden, Colorado. Over 4,000 tons of rock have been used in test work that has resulted in a technically feasible process for treating alunite.

The feasibility of producing alumina from alunite is being demonstrated elsewhere in the world as well. In the U.S.S.R., alunite is mined in Azerbaijan and processed to alumina and other products at the town of Kirovabad. This alunite-to-alumina operation, which started in the mid-1960s, produces approximately 200,000 tons per year of alumina. The Kirovabad plant is currently undergoing expansion to permit annual production of about 500,000 tons of alumina. The plant produces sulfate of potash and sulfuric acid as coproducts and, reportedly, vanadium as a byproduct.

The Barite Iran Company plans to develop an alunite-processing complex near Takistan, Iran, utilizing Soviet or U.S. technology. Workers at the University of Guanajuato in Mexico have developed several methods for processing a 100-million-ton alunite deposit near Salamanca.

Accessory Constituents

In the large disseminated-type alunite deposits, associated minerals are primarily derived by hypogene or supergene acidic alteration of the common rock-forming minerals or, to a lesser extent, introduced by hydrothermal fluids.) These can be classified conveniently as major (greater than 5 percent of the rock) and minor (less than 5 percent) accessory minerals.

Major Accessory Minerals

The most abundant associated mineral in most alunite deposits is quartz (SiO_2). In disseminated alunite deposits, quartz commonly makes up 50 to 70 percent of the rock. The quartz is both primary and secondary; the latter results from the breakdown of alumino-silicate minerals and from silica carried in the ore-forming solutions. In many places, the quartz forms intricate intergrowths with the alunite, suggesting either contemporaneous crystallization or complete replacement of the primary feldspars by alunite and quartz with little or no mobilization of the silica. The central parts of many alunite deposits contain larger amounts of quartz within the linear or circular central vents through which the altering fluids migrated. Commonly, quartz is the only major associated mineral in alunite deposits.

In the outer parts of areas of strong alunite alteration, clay minerals such as kaolin, nacrite, dickite, and halloysite are in many places a major fraction of the rock mass.

In places within some alunite deposits, tridymite, ferric oxides, amorphous and hydrated silica (volcanic glass or opal), pyrophyllite, sericite, and feldspar may exceed 5 percent of the rock. These occurrences are primarily of mineralogical interest and do not represent large fractions of any known alunite deposits.

Minor Accessory Minerals

The most common minor accessory constitutents of alunite deposits are clay minerals, various forms of silica, volcanic glass, and iron oxides. The iron occurs as hematite (Fe_2O_3), goethite ($Fe_2O_3{\bullet}H_2O$), and in some places as jarosite [$KFe_3(OH)_6(SO_4)_2$], an alunite-like mineral in which iron substitutes for aluminum in the crystal lattice. In some alunite deposits, pyrite (FeS_2) occurs with the alunite, generally only in the deeper or in the peripheral parts of a deposit.

Small amounts of other minerals identified in several deposits include pyrophyllite, diaspore, feldspar, zeolite, gypsum, apatite, andalusite, chlorite, boehmite, gibbsite, zunyite, and possibly bayerite. Most of these minerals are probably alteration products, but some (e.g., feldspar) are probably constituents of the original rock before alteration.

Trace Elements

Table 5.5 summarizes the common ranges of concentration of 48 elements in 50 areas of alunite alteration in the western United States.

In general, the abundances of minor elements and heavy metals are about equal to or less than those of acidic-to-intermediate igneous rocks. This is attributed by Hall to a flushing effect by the strongly acidic hydrothermal fluids that leached out soluble alkalies and trace-element constituents, while metasomatically altering the volcanic or subvolcanic host rock.

Where alunite and metallic ore deposits occur together, the amounts of ore metals found in the alunite are in many places anomalously high. Thus, alunite associated with porphyry copper deposits commonly has high Cu, Pb, Zn, Mo, and Ag values. Similarly, alunite associated with mercury deposits has higher values of Hg, As, Ba, etc. Alunite deposits near gold veins may contain anomalously high gold concentrations.

Mining and Processing and Related Products and Wastes

The economics of alumina production are such that for any form of alumina raw material relatively large-scale operations are more

TABLE 5.5 Accessory Elements in Alunite Deposits in the Western United States

Element	Concentration (in ppm except where % is noted)	Abundance in Granitic Rocks	Element	Concentration (in ppm except where % is noted)	Abundance in Granitic Rocks
Be	* <1-2	5	Ag	<1-2	0.04
B	2-15	15	Cd	<20	0.2
F	400-3,000	850	In	<10	0.1
Na	0.10-1.50%	2.77%	Sn	<5-10	3
P	200-2,000	700	Sb	<200	0.2
Ca	0.2-0.5%	1.58%	Te	<2,000	0.002
Sc	<5-10	5	Ba	<100-2,000	600
Ti	1,000-4,000	2,300	Ce	<200	46
V	50-350	20	Pr	<100	5.5
Cr	10-200	4	Nd	<70	24
Mn	10-250	400	Sm	<100	6.5
Fe	0.5-2.5%	2.7%	Eu	<100	1.1
Co	<5	1	Yb	<1	2.7
Ni	<5-50	0.5	Hf	<100	4
Cu	10-200	10	Ta	<500	3.5
Zn	5-200	40	W	<50	2
Ga	10-200	18	Re	<50	0.05
Ge	<10	1.5	Au	<0.001-0.01	0.004
As	<10-30	1.5	Hg	0.02-1	0.08
Sr	200-800	285	Tl	<50	0.75
Y	<10-70	40	Pb	10-130	20
Zr	50-400	180	Bi	<10	0.18
Nb	<10-40	20	Th	<200	17
Mo	<1-10	2	U	<500	4.8

* "<" denotes lowest limit of detection by the analytical method employed, which included x-ray fluorescence, emission spectrography, atomic absorption and wet chemical procedures.

SOURCE: Unpublished data from Robert B. Hall, USGS, and others.

attractive. Thus, the following discussion assumes a large disseminated alunite deposit as a resource of alumina and other saleable products.

Mining

The known major occurrences of alunite in the United States are all exposed at the earth's surface, and though it is likely that there are many buried alunite deposits, surface mining appears to be the likely technique for the foreseeable future. Moreover, alunite ore is generally moderately hard and requires drilling and blasting, as practiced in open-pit mining used in the porphyry copper industry, for example.

Processing

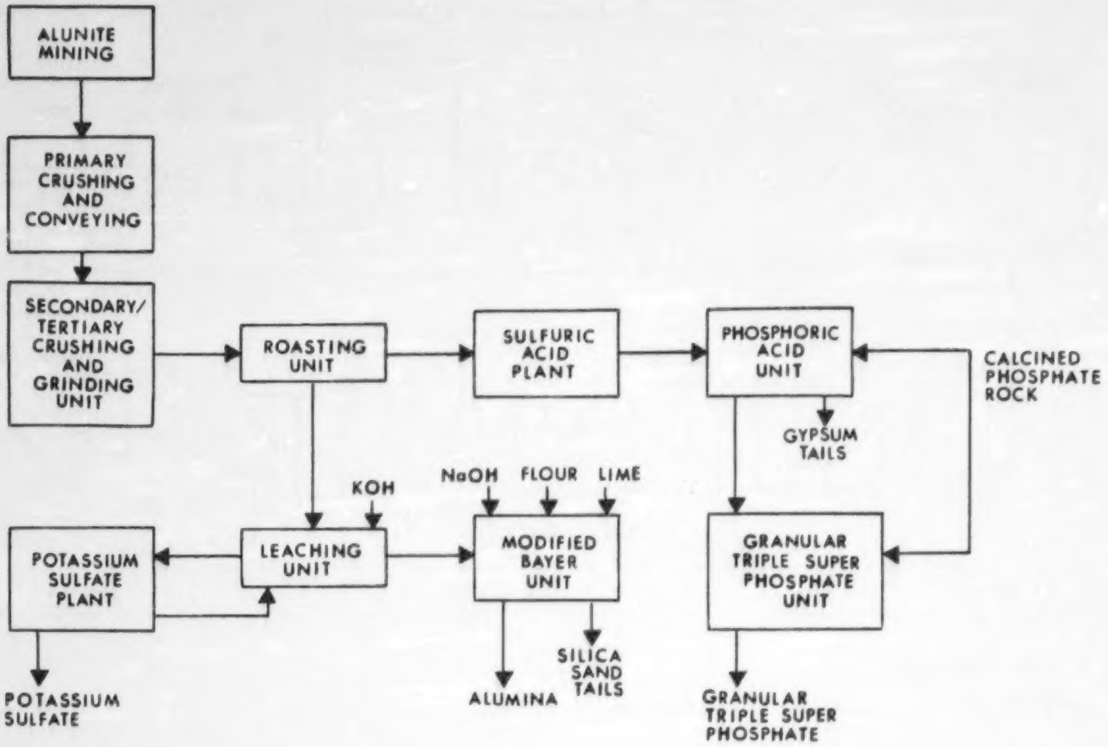
There are two general groups of processes for treating alunite: those using a caustic leach, such as the Alumet and Russian processes, and those using an acid leach, such as the UG and Kalunite processes.

The Alumet and Russian Processes These processes are quite similar. In both, the ore is crushed and ground and then roasted to drive off water of crystallization and sulfur oxides (which are converted to sulfuric acid). In the Alumet process, shown in Figure 5.10, the roasted ore is leached in a weak alkaline solution and the sulfate of potash removed by crystallization. The residue from this weak alkaline leach is sent into a modified Bayer circuit, and typical Bayer cell-grade alumina can be produced. The Russian process dissolves both sulfate of potash and alumina and uses selective precipitation to recover each product. Other caustic-leach processes have been found to be feasible, including alternatives that eliminate the roasting steps.

Ores containing clays inhibit the processing of alunite by the caustic method since they are caustic consumers. Likewise, cristobalite, a form of silica that is a major constituent of some alunite deposits, can also be a caustic consumer.

UG Process This process, developed at the University of Guanajuato, Mexico, is illustrated in Figure 5.11. Ore is crushed to -1/2 inch mesh fragments, roasted to drive off the water of crystallization, ground to -60 mesh size, and leached with ammonia to remove the potassium sulfate and the sulfate attached to the alumina. The solid residue is reacted in water with sulfur dioxide to form soluble aluminum sulfite. The remaining solids are reacted with sulfuric acid, forming aluminum sulfate in solution. The aluminum sulfate solution is boiled with the aluminum sulfite solution and a mixture of basic aluminum sulfates and aluminum hydrates is precipitated. This precipitate is filtered, washed, and calcined to produce alumina. Possible variations of the above process include a caustic digestion of alumina following the ammonia leach of potassium sulfate (Lopez 1977).

Kalunite Process The Kalunite process developed and used by Kalunite, Incorporated, during and after World War II, involves crushing,


ALUNITE MINING
PRIMARY CRUSHING AND CONVEYING
SECONDARY/ TERTIARY CRUSHING AND GRINDING UNIT
ROASTING UNIT
SULFURIC ACID PLANT
PHOSPHORIC ACID UNIT
CALCINED PHOSPHATE ROCK
GYPSUM TAILS
KOH
NaOH
FLOUR
LIME
POTASSIUM SULFATE PLANT
LEACHING UNIT
MODIFIED BAYER UNIT
GRANULAR TRIPLE SUPER PHOSPHATE UNIT
SILICA SAND TAILS
POTASSIUM SULFATE
ALUMINA
GRANULAR TRIPLE SUPER PHOSPHATE

SOURCE: NRC (1977).

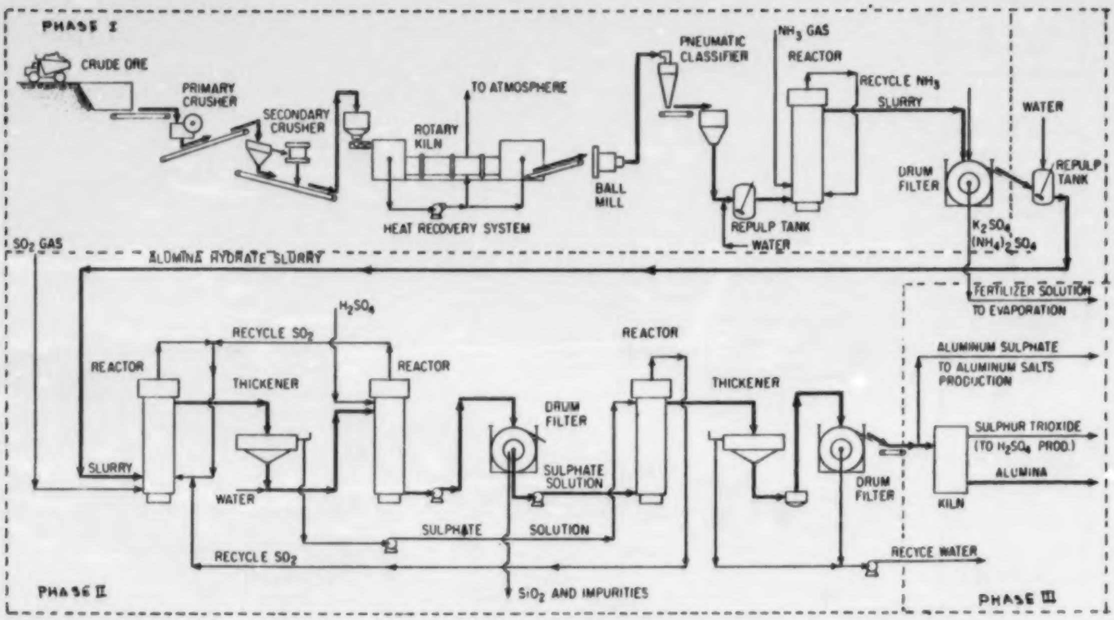
FIGURE 5.10 Generalized Alumet process flowsheet.

grinding, and roasting alunite ore to remove water of crystallization. The roasted ore is then leached with sulfuric acid and a potassium alum is crystallized. The potassium alum is roasted at a suitable pressure and temperature to form a basic alum, which can then be calcined to produce potassium sulfate and alumina (Fleischer 1944).

Products and Byproducts

The principal product of alunite is alumina. The Alumet process was designed to produce "sandy" alumina (for which most U.S. aluminum smelters are designed). The Russian process may also be able to produce "sandy" alumina. Other processes produce a "floury" or fine-grained alumina that requires different handling at the smelter. Each of these processes also produces potassium sulfate as a coproduct. In the Alumet process, approximately 1 ton of potassium sulfate is produced for every 2 tons of alumina.

Most of the processing schemes can also make sulfuric acid as a byproduct. The Alumet process involves making slightly less than 1 ton of sulfuric acid for each ton of alumina produced. This acid is used to react with phosphate rock to produce phosphate fertilizers. It is


PHASE I
CRUDE ORE
PRIMARY CRUSHER
SECONDARY CRUSHER
ROTARY KILN
TO ATMOSPHERE
HEAT RECOVERY SYSTEM
BALL MILL
PNEUMATIC CLASSIFIER
NH_3 GAS
REACTOR
RECYCLE NH_3
SLURRY
WATER
DRUM FILTER
REPULP TANK
REPULP TANK
WATER
K_2SO_4
$(NH_4)_2SO_4$
SO_2 GAS
ALUMINA HYDRATE SLURRY
FERTILIZER SOLUTION
TO EVAPORATION
H_2SO_4
RECYCLE SO_2
REACTOR
THICKENER
REACTOR
DRUM FILTER
REACTOR
THICKENER
ALUMINUM SULPHATE
TO ALUMINUM SALTS PRODUCTION
SULPHUR TRIOXIDE
(TO H_2SO_4 PROD.)
ALUMINA
KILN
SLURRY
WATER
SULPHATE SOLUTION
DRUM FILTER
SULPHATE
SOLUTION
RECYCLE SO_2
RECYCE WATER
PHASE II
SiO_2 AND IMPURITIES
PHASE III

SOURCE: Lopez (1977).

FIGURE 5.11 Generalized U.G. Process flowsheet.

believed that the Soviet plant uses sulfuric acid for similar purposes. The Kalunite process uses the sulfuric acid that it produces to react with roasted alunite.

The Soviets reportedly produce vanadium pentoxide as a minor byproduct. Alumet has not designed circuits for the recovery of byproducts, but studies are planned to determine whether vanadium or gallium might be profitably extracted from the modified Bayer circuit. In areas where alunite deposits are associated with metallic mineral deposits (e.g., gold, copper, mercury) the recovery of a byproduct may be practical.

Waste Products

Waste from alunite mining consists primarily of overburden and of waste rock included within the alunite ore. This spoil is usually stored close to the mining operation to avoid excessive handling, and since it is exposed to weathering, oxidation and leaching can occur. Oxidation of the minor amounts of pyrite (1 to 2 percent) could form sulfuric acid and soluble ferric sulfate. Precautions should be taken to prevent such products from becoming pollutants. Other acid-soluble accessory elements exist in such low concentrations in alunite deposits (see Table 5.5) that it is considered unlikely that significant environmental pollution from these elements would result. Revegetation of spoil piles and mined-out areas would depend on climate, availability of soils, and other factors. Most of the alunite deposits considered in this study are in areas of relatively low precipitation; this reduces the potential for complete revegetation, but at the same time it also reduces the probable effects of oxidation and leaching. Studies of the possibilities for both revegetation and leaching should be made at each proposed new alunite operation.

Wastes will vary depending on the processing method used. The Alumet process produces a solid waste, predominantly silica, that can be slurried to a tailings pond for disposal. Because Alumet plans to process phosphate rock with the sulfuric acid produced from alunite, a gypsum tailings pond will be necessary. Table 5.6, taken from the Draft Environmental Impact Statement (EIS) prepared by the Bureau of Land Management (BLM) for the Beaver County, Utah, Alunite Project, shows the amounts of wastes generated at various stages of processing, including the air emissions. These data are for a plant that would produce 500,000 short tons of alumina per year.

Process tailings from the proposed Alumet plant in Beaver County would probably contain trace elements and heavy metals in only very small quantities, and therefore no problems are foreseen by the company, the BLM team that prepared the EIS, or the Environmental Protection Agency, which reviewed the proposed waste discharge. The slurry-water composition (Table 5.6) indicates that the water will be mildly alkaline but will not contain significant concentrations of heavy metals or toxicants in solution. This water will be recycled for slurrying with additional solid waste, and fresh water will be added to compensate for evaporation; thus, a closed system will be maintained.

Off-gases from roasting of the ore were monitored by Alumet during pilot-plant studies at Golden, Colorado. Under current EPA and Utah state guidelines, the sulfur dioxide and particulate emissions from ore-roasting and from coal-fired power- and steam-generating plants create the largest potential sources of environmental degradation.

Much less is known about the wastes generated by other alunite processes. Because the Russian process consists of a series of roasts and a caustic leach similar to those used in the Alumet process, it is believed that the wastes will also be similar.

The acid-alumina-leach processes (UG process and Kalunite process) may solubilize some elements that would not be taken into solution by the caustic leaches (Fleischer and Glasser 1951). Additional studies will probably be required to identify the accessory constituents associated with these processes and to assess possible environmental effects. However, if a closed system is maintained between plant and tailings pond, environmental degradation could be minimized or perhaps eliminated.

Conclusions and Recommendations

Alunite is the only non-bauxitic source of cell-grade alumina in the world today in commercial production primarily for alumina. The Soviet plant at Kirovabad has been in operation for more than 10 years and is currently expanding production capability.

The Alumet process has been pilot-tested and has demonstrated technical feasibility for production of cell-grade alumina. Ore reserves have been proved by drilling, the final environmental impact

TABLE 5.6 Summary of Daily Emission and Tailings from Alumet Processing Plant Complex[a]

Operation or Plant	Air Emissions, pounds per day				Tail Solids, dry		Tail Solution	
	Particulate	SO_2	NO_x	Fluoride	Tons	Composition, %	Tons	Composition, %
Crushing and grinding	2,100	--	--	--	--	--	--	--
Roasting	3,800	22,800	17,000	--	--	--	--	--
Sulfuric acid plant	--	2,400	--	--	--	--	--	--
Potassium sulfate plant	350	--	--	--	--	--	850	12% potassium sulfate, 5% sodium sulfate, 0.23% alumina, 0.33% sodium hydroxide
Alumina plant	750	3,200	4,800	--	7,800	91% silica, 3% alumina, 6% iron oxide and other hydrated lime and silica compounds	11,700	0.3% sodium carbonate, 0.23% alumina, 0.33% sodium hydroxide
Phosphate[c/] fertilizer plant	2,100[b/]	400	--	420	5,000	87% gypsum, 7% silica, 4% phosphate rock, 2% fluorides	1,800	1% sulfuric acid, 1% phosphoric acid, 0.5% fluorides
Aluminum fluoride[c/] plant	250	--	--	32	30	Silica with 3% aluminum fluoride	45	Gypsum pond solution, spent leach liquor-3% aluminum fluoride
Power and steam generation plant	3,500	9,500	21,000	--	220	Ash	450	Boiler blowdown water
SO_2 Scrubber	--	--	--	--	700	Unreacted lime, calcium sulfite, and calcium sulfate	2,800	Silica pond solution
Support facilities	--	--	--	--	3	Trash and garbage	1,200	Sewage
Total	12,850	37,900	42,800	452				

a/ Data not included for bleed streams from several wet scrubbers.

b/ Ammonia

c/ These portions of the plant are planned by Alumet for the Beaver County Alunite Project and may not be included in alunite processing plants in other areas.

SOURCE: U.S. DOI (1976).

study has been completed, and governmental approval for construction is expected during 1980 for Alumet's Beaver County, Utah, alunite project. The UG process has been tested in the laboratory and in a small pilot plant. However, assessment of the environmental effects of the UG process will depend on further study. The Kalunite process was demonstrated in the late 1940s and proved that aluminum could be made from Kalunite alumina. However, this process appears less attractive economically than the other three.

All of the mining and waste disposal techniques necessary for alunite mining are well developed in other sectors of the mining industry, and most of the technology to be used in processing is also used in other metallurgical applications.

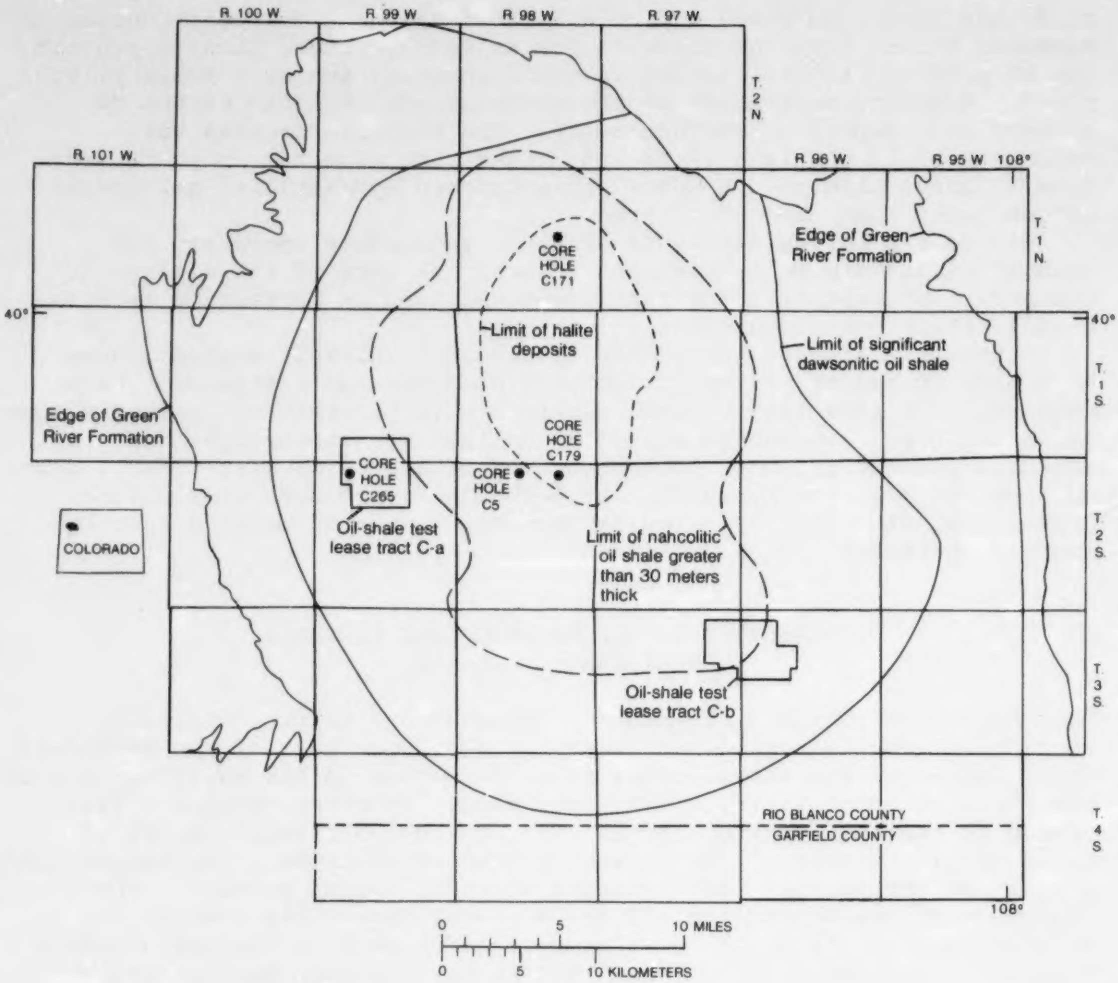
Although a significant number of accessory element analyses have been made on alunite deposits, continuing data acquisition will be required. If potentially toxic substances (e.g., mercury) exist in some deposits, these substances should be defined and appropriate control measures planned prior to production. Some elements, particularly gold, gallium, copper, and vanadium, are potential byproducts of alunite processing, and recovery circuits for them can be integrated into the overall operation.

DAWSONITE IN OIL SHALE OF THE PICEANCE CREEK BASIN, COLORADO

Dawsonite [$NaAl(OH)_2CO_3$], nahcolite ($NaHCO_3$), and halite ($NaCl$) are commingled with high-grade oil shale in the lower part of the Parachute Creek Member of the Eocene Green River Formation in the northern part of the Piceance Creek Basin, Rio Blanco County, Colorado (Figure 5.12). Dawsonite-bearing rocks occupy an area of about 500 square miles in parts of 24 townships. The dawsonite content of these rocks ranges from 1 to 25 weight percent, and averages about 10 weight percent. The thickness of the dawsonitic oil shale ranges from a few feet at the northern end of the Basin to as much as 1,100 feet at the Basin center. Dawsonitic oil shale 500 or more feet thick underlies approximately 150 square miles in the northern part of the Basin. This zone averages about 3 weight percent extractable alumina and contains within it a 25-foot-thick unit averaging about 5 weight percent alumina; this is the highest-grade unit of significant thickness and extent in the Basin. In the central part of this deposit, the dawsonitic rocks are 1,000 to 2,000 meters below the surface.

Mineralogy

The fine-grained mineral matrix of dawsonitic oil shale comprises dawsonite, dolomite, quartz, potassium and sodium feldspar, and small amounts of pyrite/pyrrhotite, calcite, and illite. Scattered coarse crystalline aggregates and fine- to coarse-grained beds of nahcolite are also abundant. Toward the basin's center of deposition, there are several thick units of interbedded halite and nahcolite in the upper part of the dawsonitic sequence. Toward the margins of the basin,


R. 100 W.
R. 99 W.
R. 98 W.
R. 97 W.
T. 2 N.
R. 101 W.
R. 96 W.
R. 95 W.
108°
T. 1 N.
Edge of Green River Formation
CORE HOLE C171
40°
40°
Limit of halite deposits
Limit of significant dawsonitic oil shale
T. 1 S.
Edge of Green River Formation
CORE HOLE C179
CORE HOLE C265
CORE HOLE C5
COLORADO
Oil-shale test lease tract C-a
Limit of nahcolitic oil shale greater than 30 meters thick
T. 2 S.
T. 3 S.
Oil-shale test lease tract C-b
RIO BLANCO COUNTY
GARFIELD COUNTY
T. 4 S.
108°
0
5
10 MILES
0
5
10 KILOMETERS

SOURCE: NRC (1977).

FIGURE 5.12 Areas of dawsonitic oil shale, nahcolite, and halite in the Green River Formation of the Piceance Creek Basin, northwest Colorado (all boundaries approximate).

illite, analcime, and probably calcite are major constituents of the oil shale.

The average mineral composition of the unleached and illite-free part of the dawsonitic oil shale penetrated in a core hole near the basin center is given in Table 5.7 (Dyni 1974; J.R. Dyni, unpublished data 1977).

Dawsonite and Excess Alumina

Dawsonite, a white or colorless acid-soluble mineral, generally occurs as stubby to elongate crystals 2 to 20 micrometers long (averaging less than 10) disseminated in the oil shale. In places, it also occurs in thin streaks and small fibrous aggregates (Smith and Milton 1966, and Desborough and Pitman 1974). An aluminum-bearing substance that appears amorphous to x-rays, termed "excess alumina," is coextensive with dawsonite in amounts ranging up to 5 weight percent alumina. It dissolves in acids and bases and has a differential-thermal-analysis curve similar to that of gibbsite (Smith and Young 1975). The identity of this compound remains elusive, but considering the abundance of organic matter associated with it, it could be an organo-aluminum compound; this possibility has not been investigated.

Accessory Constituents

The concentrations of accessory constituents in the Colorado oil shale deposits and their possible environmental effects, as a result of retorting and of the accumulation of large volumes of spent shale, have come under intensive study in the past few years by several federal agencies, universities, and research institutes. The results are beginning to be published. The accumulation of data about accessory elements in the dawsonitic oil shale will probably lag behind that for the more accessible Mahogany Zone of the Green River Formation, but it is anticipated that this data bank will continue to grow.

Poulson et al. (1977) give the abundances of 63 elements in dawsonitic oil shale, as well as elemental abundances in shale oil and

TABLE 5.7 Average Mineral and Organic Content of Dawsonite Shale (weight percent)

	Mean	Range
Nahcolite	17.2	0 -77.3
Dawsonite	9.5	0.4-24.1
Dolomite (includes some calcite)	21.8	6.4-41.9
Potassium feldspar (includes minor illite)	9.1	0 -19.9
Sodium feldspar	9.0	0 -35.0
Quartz	13.5	1.7-44.5
Kerogen	18.9	4.2-48.6
Pyrite/pyrrhotite	∿1	?
Total	100	

SOURCE: Dyni (1974); Dyni, unpublished data (1977).

in water obtained from retorting non-dawsonitic (Mahogany Zone) oil shale. Desborough and Pitman (1974) and Desborough et al. (1976) have studied the abundances and mineral residences of selected elements in a thin bed of rich oil shale from the lower part of the dawsonite zone. Environmentally important elements, including cadmium, antimony, arsenic, mercury, selenium, fluorine, and boron, have been monitored by the lessees of federal oil shale lease tracts C-a and C-b, which are located near the margins of the dawsonitic oil shale deposits (Figure 5.12). Analyses of shales from the lease tracts, as well as data from various published and unpublished sources, were recently summarized by Dean (1976). However, many of these data pertain to oil shale from the Mahogany Zone, which lies many meters above the dawsonite zone, and therefore may not be representative of the entire oil shale deposit nor of the dawsonitic rocks.

The abundances of 62 elements in dawsonitic oil shale are listed in Table 5.8. The data for the first group of 35 elements listed in the table were provided by J.R. Dyni and J.R. Donnell from analyses made in the Denver laboratories of the U.S. Geological Survey; the data for the remaining group of 27 elements are from Poulson et al. (1977). The analyses summarized in Table 5.8 were made on samples of fresh, unweathered dawsonitic oil shale obtained from four core holes (locations shown on Figure 5.12). Accurate values for total sodium and magnesium are still not available.

Dawsonitic oil shale is not notably enriched in metals, with the exception of molybdenum. Compared with elemental abundances in carbonate rocks and shales (Table 5.8), dawsonitic oil shale is enriched in Mo, Pr, Cs, Ag, Se, S, Cl, As, F, Si, Ta and P by factors ranging from 1.1 to 10, with the molybdenum enrichment being the greatest. The amounts of manganese and bromine and of several trace elements are smaller in dawsonitic oil shale than their average abundances in carbonate rocks and shales. Bromine, as bromide ion, is locally concentrated in halite in amounts of as much as 182 parts per million (Dyni et al. 1970).

The mineral residences of some of the elements listed in Table 5.8 are those suggested by Desborough et al. (1976), Dean (1976), Milton (1971), and Dyni (unpublished data, 1977). The actual minerals in which they reside have not been determined for these elements. Such metals as Mo, Zn, Ni, Cu, Cr, and V are known to have organic affinities. The role of kerogen in concentrating these metals has not been investigated.

Pyrite is thought to be the mineral residence of many of the trace metals. If this is true, study of the vertical and lateral distribution of total sulfur may be useful in isolating parts of the oil shale enriched in sulfide minerals and associated trace metals.

Mining and Processing

The technology for recovering alumina and nahcolite from dawsonitic oil shale is largely new, as neither mineral has previously been mined commercially. Process designs seem to be compatible with conventional methods of retorting oil shale and are based on caustic leaching of the retorted shale (see Figure 5.13). Haas and Atwood (1975) have described one method and Weichman (1974b) has described another. Silica contamination, buildup of soluble wastes in the leaching solution, and

TABLE 5.8 Abundances of Selected Elements in Dawsonitic Oil Shale

Atomic Number	Element	In Parts Per Million (except as noted)						Difference 2/	Probable Mineral Site of Element
		Range	Mean	Standard Deviation	Lower Detection Limit of Method	Average Abundances in Sedimentary Rocks 1/			
						Carbonates	Shales		
		NEW DATA IN THIS REPORT							
5	B	<20-200	<26	42	20	20	100	0	K-feldspar?, searlesite
9	F	300-2,200	968	491		330	740	+	Cryolite, fluorite
13	Al	0.5-8.0%	3.9%	1.5%		0.42%	8.0%	0	Feldspars, dawsonite, excess alumina, analcime, illite
14	Si	1.9-26.2%	13.5%	4.48%		2.4%	7.3%	+	Quartz, feldspars, analcime, illite
16	S	1,000-49,000	12,400	7,200	100	1,200	2,400	+	Pyrite, kerogen
17	Cl	40-650	266	180		150	180	+	Halite
19	K	0.3-2.5%	1.4%	0.4%		0.27%	2.66%	0	K-feldspar, illite
19	K^{40}	(7-24)	(11)	(5)					K-feldspar
20	Ca	0.6-10.7%	5.2%	1.9%		30.23%	2.21%	0	Dolomite, calcite
21	Sc	<5-15	<8	3	5	1	13	0	?
22	Ti	200-2,000	1,218	452	2	400	4,600	0	?
23	V	20-200	120	45	7	20	130	0	Kerogen
24	Cr	7-70	43	18	1	11	90	0	?
25	Mn	20-300	195	77	1	1,100	850	-	Dolomite, siderite
26	Fe	2,700-37,600	19,800	7,200	~100	3,800	47,200	0	Pyrite, dolomite, siderite, illite
27	Co	<5-20	<9	5	5	0.1	19	0	Pyrite
28	Ni	<5-150	<25	19	5	20	68	0	Pyrite
29	Cu	5-100	38	23	1	4	45	0	Pyrite
31	Ga	<5-30	<13	8	5	4	19	0	?
33	As	12-36	24	9		1	13	+	Pyrite, kerogen?
35	Br	<1-7.8	2.7	3.3	1	6.2	4	-	Halite
38	Sr	20-720	335	115		610	300	0	Dolomite, calcite
39	Y	<10-70	<11	8	10	30	26	-	?
40	Zr	<10-50	<31	12	10	19	160	0	Zircon
42	Mo	<3-200	<25	28	3	0.4	2.6	+	Pyrite
48	Cd	?	<1	?		0.035	0.3	- or 0	Sulfite minerals
51	Sb	0.9-2.5	1.6	0.6		0.2	1.5	+	?
53	I	0.7-3.3	1.6	1.2		1.2	2.2	0	Kerogen?
56	Ba	70-2,000	333	249	2	10	580	0	Carbonate mineral?
70	Yb	<1-5	<1.3	0.6	1	0.5	2.6	0	?
80	Hg	0.09-0.19	0.14	0.03		0.04	0.4	0	?
82	Pb	<10-70	<20	16	10	9	20	0	Pyrite
88	Ra^{226}	(0.7-1.8)	(1.1)	(0.4)					?
90	Th	4-6	5	1		1.7	12	0	Pyrite?
92	U	2-5	4	2		2.2	3.7	0	Pyrite
	Water	0.2-8.3	2.6	1.7					Nahcolite, dawsonite, analcime, kerogene

TABLE 5.8 (Continued)

Atomic Number	Element	In Parts Per Million (except as noted)						Difference2/	Probable Mineral Site of Element
		Range	Mean	Standard Deviation	Lower Detection Limit of Method	Average Abundances in Sedimentary Rocks1/			
						Carbonates	Shales		
SELECTED DATA FROM POULSON AND OTHERS (1977)									
3	Li	5.7-100	41	28		5	66	0	Carbonate
4	Be	<0.18-2.2	<0.89	0.64		0.X	3	0	?
15	P	510->5,000	>3,114	1,729		400	700	+	?
30	Zn	12-60	35	19		20	95	0	Wurtzite
32	Ge	0.37-1.9	1.1	0.58		0.2	1.6	0	?
34	Se	0.78-4.7	1.8	1.3		0.08	0.6	+	Sulfide or iron selenide
37	Rb	11-110	63	32		3	140	0	Carbonate
41	Nb	1.4-20	8.8	6.1		0.3	11	0	?
47	Ag	0.12-0.40	0.29	0.14		0.0X	0.07	+	Sulfite
50	Sn	0.35-2.2	1.4	0.67		0.X	6.0	0	?
55	Cs	0.43-11	5.2	3.7		0.X	5	+	?
57	La	1.1-37	19	11		X	92	0	?
58	Ce	4.0-80	43	24		11.5	59	0	?
59	Pr	0.60-16	7.1	5.0		1.1	5.6	+	?
60	Nd	2.4-29	15	8.7		4.7	24	0	?
62	Sm	<0.50-5.1	<2.8	1.4		1.3	6.4	0	?
63	Eu	<0.18-1.8	<0.94	0.56		0.2	1.0	0	?
64	Gd	<0.06-0.71	<0.40	0.22		1.3	6.4	-	?
65	Tb	<0.13-1.1	<0.55	0.37		0.2	1.0	0	
66	Dy	<0.27-3.1	<1.6	0.87		0.9	4.6	0	?
67	Ho	<0.05-0.44	<0.22	0.14		0.3	1.2	-	?
68	Er	<0.08-0.28	<0.18	0.08		0.5	2.5	-	?
69	Tm	<0.03-0.09	<0.06	0.03		0.04	0.2	0	?
71	Lu	<0.15-0.50	<0.24	0.13		0.2	0.7	0	?
72	Hf	<0.55-2.5	<1.3	0.73		0.3	2.8	0	?
73	Ta	0.43-4.8	1.4	1.4		0.0X	0.8	+	?
74	W	<0.32-2.9	<1.2	0.94		0.6	1.8	0	?
81	Tl	<0.12-1.4	<0.42	0.42		0.0X	1.4	0	?

1/ Data from Turekian and Wedepohl (1961). X indicates order of magnitude where data are insufficient.

2/ The symbol (-) indicates that the mean value of the element in the oil shale is less than the average for both carbonates and shales; (O) indicates the mean value lies between the two averages; and (+) indicates the mean value is larger than both averages.

NOTES: The values reported for uranium, thorium, ^{40}K, and ^{226}Ra were obtained from 9 samples that are composites of 29- to 37-meter lengths of drill core spaced evenly between depths of 444 and 791 meters below ground level in core hole C-179*. The units for ^{40}K and ^{226}Ra are pCi/g. The precision and accuracy are within 10 percent of the values reported. The analyses were made by gamma-ray spectroscopy at Oak Ridge National Laboratory and were provided through the courtesy of Dr. William A. Goldsmith.

Analyses of arsenic, cadmium, mercury, antimony, and eight of 50 analyses of fluorine were made for 8 samples that are composites of 10- to 27-meter lengths of drill core spaced evenly between depths of 133 and 290 meters below ground level in core hole C-265*. Arsenic, cadmium, and mercury were determined by atomic absorption, antimony by the Rhodamine-B method, and fluorine by specific-ion electrode. These data were provided by panel member J. R. Donnell, U. S. Geological Survey.

Analyses of the remaining elements and 42 of the fluorine analyses were made for selected samples, or for all samples (for some elements), of a suite of 308 samples that are composites of 0.6- meter lengths of drill core spaced evenly between depths of 561 and 753 meters below ground level in core hole C-5*. Sulfur, iron, strontium, chlorine, bromine, and iodine were determined by X-ray fluorescence; and the remaining elements by 6-step emission spectroscopy.

The values for water are those obtained from the Fischer assay method after retorting the 308 samples from core hole C-5 at about 500°C.

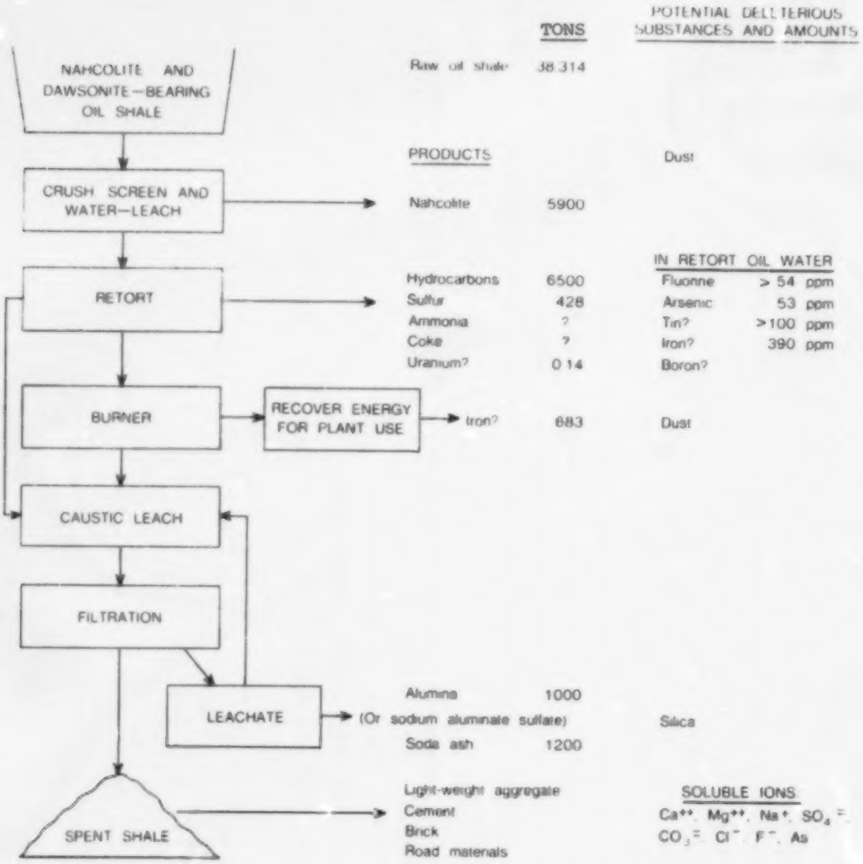
*See Figure 2.10 for core-hole locations.

SOURCE: NRC (1977) and sources indicated above and on the Table.

pH level are believed to be controllable. The technology of these processes has probably advanced to the demonstration-plant stage. The feasibility of recovering alumina from dawsonitic oil shale retorted by in situ methods cannot yet be evaluated because data are insufficient.

In the proposed process, the extractable alumina contained in the retorted oil shale would be solubilized as sodium aluminate in a mild caustic (pH of 10 to 12) water solution of sodium hydroxide or sodium carbonate. The alumina can then be precipitated as aluminum hydroxide by conventional methods of carbonation of the filtered leachate, and the aluminum hydroxide can be calcined to alumina.

Both retorted and burned dawsonitic oil shale can be leached for their alumina content. Retorted oil shale contains as much as 3 to 5 weight percent organic carbon. Burned oil shale contains less than .1 percent organic carbon, and is the residue from retorted oil shale that has been burned to recover its energy.


TONS
POTENTIAL DELETERIOUS SUBSTANCES AND AMOUNTS
NAHCOLITE AND DAWSONITE-BEARING OIL SHALE
Raw oil shale 38,314
PRODUCTS
Dust
CRUSH SCREEN AND WATER-LEACH
Nahcolite 5900
RETORT
Hydrocarbons 6500
Sulfur 428
Ammonia ?
Coke ?
Uranium? 0.14
IN RETORT OIL WATER
Fluorine > 54 ppm
Arsenic 53 ppm
Tin? >100 ppm
Iron? 390 ppm
Boron?
BURNER
RECOVER ENERGY FOR PLANT USE
Iron? 683
Dust
CAUSTIC LEACH
FILTRATION
LEACHATE
Alumina 1000
(Or sodium aluminate sulfate)
Soda ash 1200
Silica
SPENT SHALE
Light-weight aggregate
Cement
Brick
Road materials
SOLUBLE IONS
Ca⁺⁺, Mg⁺⁺, Na⁺, SO₄⁼, CO₃⁼, Cl⁻, F⁻, As

SOURCE: NRC (1977).

FIGURE 5.13 Flow chart for mining and processing dawsonitic oil shale for extractable alumina (based on 2.90 weight percent extractable alumina and 90 percent product recovery).

The major problem in the alumina-leaching process appears to be the dissolution of silica and its contamination of the precipitated alumina. Analcime could contribute much soluble silica, especially toward the margins of the dawsonite deposits, where it is more abundant. A short contact time between the leaching solution and the spent shale, and control of pH, are believed to be important factors in controlling the solubility of silica.

Products and Byproducts

The potential products from processing dawsonitic oil shale are alumina for the manufacture of aluminum metal, or, alternatively, a sodium-aluminate/aluminum-sulfate product for treatment of waste waters (B.E. Weichman in Rothberg 1974, Appendix 2:40-41). Other coproducts include nahcolite for the removal of sulfur and nitrogen oxides from stack gases, soda ash, and the conventional products of oil shale, including hydrocarbons, elemental sulfur, and ammonia. The quantities of some of these products are estimated in Figure 5.13.

Although the data in Table 5.8 suggest that most accessory elements are in concentrations too low to be economic, other factors should be considered. The enormous size of the oil shale resource and the mining and processing methods used could enhance the economic recovery of trace elements. The lateral distribution of accessory elements in dawsonitic oil shale is not yet well known; metal values may increase toward the basin margins, as has been suggested for similar rocks in the Uinta Basin of Utah (Dyni 1976).

Poulson et al. (1977) reported significant enrichment of uranium (200x) in waters and oils obtained from retorting nondawsonitic oil shale of the Green River Formation. Presumably, the uranium is mobilized during retorting and is concentrated in the retort fluids. The uranium is of special interest because it may be recoverable.

Perhaps the greatest challenge to the oil shale technologist is to find as many possible uses for the spent shale as are economically feasible. It has been suggested that lightweight aggregate, portland cement, brick, road construction materials (including aggregate and base materials), glass, and glass-ceramics might be made from spent shale (Ashland Oil Company and Shell Oil Company 1976, and Chavez 1977).

If the dawsonitic oil shale deposits are developed by open-pit mining, vast quantities of overburden will be moved. Part of this overburden consists of siltstones and other fine-grained rocks of the Eocene Uinta Formation that contain little or no organic matter. Because the emphasis has been on oil shale development, virtually nothing is known about the mineralogy of these rocks or whether they contain accessory materials of potential economic interest.

Waste Materials

Based on processes outlined by Haas and Atwood (1975) and by Weichman (1974b), the weight of the finely pulverized spent shale should be about 60 percent of the weight of the original rock. Thus, the minerals and accessory elements not removed could be roughly doubled in amount in the spent shale. The fine-particle size of the spent shale (about 30 percent of it will pass through a no. 325 sieve) would present problems of dust control, and the rate of dissolution of minerals would be enhanced by the increased surface area.

Unrecovered sulfide minerals in the spent shale would oxidize to water-soluble sulfate. On exposure to air, much of the iron sulfide observed in fresh drill cores of dawsonitic oil shale oxidizes rapidly to soft, black, sulfate compounds. Sizeable quantities of the carbonates of calcium, magnesium, and sodium, and of sodium chloride could probably be dissolved from the spent shale, depending partly on the methods used for retorting and burning the oil shale. The pH of waters in contact with spent shale might range from 7.5 to 9 (Ashland Oil Company and Shell Oil Company 1976) or go as high as 11 (I.C. Frost, unpublished data 1948). If pH values above 10 are obtained, significant quantities of silica would be dissolved.

Some potentially noxious elements, especially fluorine and arsenic, might be mobilized in retort waters during processing or later in meteoric waters in contact with the retorted shale. Dissolution of fluoride from spent shale might be particularly troublesome because of the low solubility of fluoride minerals, which would tend to release fluoride more slowly over a longer period of time. It might be possible to flush potentially harmful elements of higher solubility (perhaps arsenic, for example) from spent shale and thus control them satisfactorily. The fluoride content of saline ground water in contact with dawsonitic oil shale in the deeper part of the basin is as high as 54 mg/l (Coffin et al. 1971). Retort waters and oils are enriched in F (54 parts per million), As (53 parts per million), Sn (>100 parts per million), Fe (77 parts per million), and B (120 parts per million), according to Poulson et al. (1977, tables 11 and 12). These elements, and perhaps others, might require special control during retorting and processing.

Conclusions and Recommendations

The mineral and organic residences, stratigraphic distributions, and associations of accessory constituents in dawsonitic oil shale, including "excess alumina," are still poorly known and in need of study. The concentrations of minerals and other accessory constituents appear to vary from the margins to the center of the basin as well as vertically through the oil shale deposits. A better understanding of these variations would permit evaluation of the oil shale for potentially useful products and would help flag those parts of the deposit that may be enriched in either valuable or deleterious substances. Accessory element data are also needed as a basis for the design of processes for the recovery and disposal of useful and deleterious substances in the oil shale.

Almost nothing is known about the mobilization and fate of accessory elements in the several processes proposed for alumina recovery. Significant concentrations of potentially harmful elements, including As, Sn, F, Fe, and B, have been reported in retort waters and in the shale oils produced. One might expect similar anomalous concentrations of these and possibly other elements in process waters used in the recovery of alumina. An effort should be made, in cooperation with research groups and interested companies, to study the mass balance, transport, and fate of accessory elements in the processing of dawsonitic oil shale for alumina.

Research into the chemistry and reactions of waters in contact with spent shale is needed. The kinds and amounts of ions dissolved by meteoric waters in contact with retorted and oxidized oil shale in several types of retorts should be compared, both before and after alumina recovery. The effects of oxidation of sulfide minerals that survive retorting should be investigated, as should the release of sulfate and associated metals to solutions. The dissolution of fluoride from spent shale should perhaps receive special attention, because of evidence of its high concentration in retort water and in ground water in contact with dawsonitic oil shale in the subsurface.

The remarkable concentration of uranium in retort fluids from Green River oil shale represents a potential resource that should be pursued. If this uranium can be mobilized in a water-soluble form, it may be relatively easy to recover.

Spent shale should be tested for use in such products as cement, brick, lightweight aggregate, glass, and similar low-unit-cost commodities. Shipping costs might restrict the market areas for most of these products, but they would be partly offset by the lower production costs of mining and milling.

Because parts of the oil shale deposits might be mined in open pits, the overburden (rocks of the Uinta Formation overlying the oil shale deposits) should be studied to determine whether possibly deleterious or useful constituents are present.

ANORTHOSITE

Anorthosite is an igneous rock characterized by a relatively high alumina content, ranging from about 25 to 30 percent. It is not likely to be exploited exclusively for aluminum in the foreseeable future, but a particular deposit might possibly be mined for recovery of aluminum and other products in a combined operation that would be economically viable. Thus, accessory constituents and potential byproducts in anorthosites could be especially important.

Anorthosite is composed primarily of plagioclase feldspar and relatively small amounts (less than 10 percent) of clinopyroxene and orthopyroxene. Minor quantities of potassium feldspar and quartz may also be present. Accessory minerals found in anorthosite include iron and titanium oxides, apatite, zircon, and sphene. Metamorphism of anorthosite intrusions has in some places formed small amounts of biotite, hornblende, garnet, and chlorite.

Anorthosites are found as large Precambrian massifs or as layers in segregated igneous intrusions. These two forms are distinguished by the difference in composition of the dominant plagioclase. In the massif-type anorthosite, the plagioclase (anorthite) varies in composition between An_{35} and An_{80}, whereas in the layered intrusive type it varies between An_{65} and An_{80}. Forms of anorthosite intrusion that are intermediate between these two types are also found.

Resources

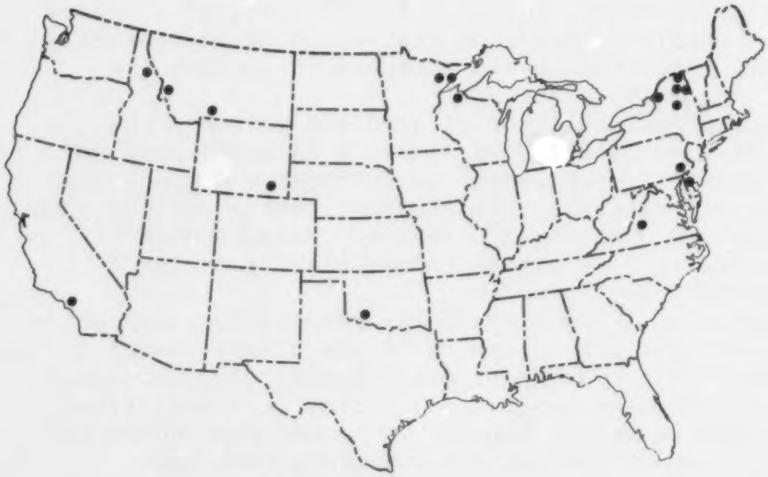
Anorthosites are widely dispersed throughout the United States. Those that are best known and most likely to be exploited are listed in Table 5.9 and located in Figure 5.14. Anorthosite bodies may range in size from small pods and stringers measured in meters to enormous intrusions underlying areas of more than 1,000 square miles. Estimates of exposed surface area and total mineable tonnages are given in Table 5.9.

Identification of the anorthosite deposits that are most suitable for exploitation depends partly on the availability of raw materials essential for the lime-soda processes, as well as the proximity of markets for cell-grade alumina and byproducts (e.g., cement). The required raw materials are limestone, fuel, and soda ash, which are found together in the western United States, primarily in Wyoming, Montana, and Idaho. The abundant supplies of coal in these states could be decisive in the possible future development of anorthosites for aluminum.

Anorthosite deposits in mountainous or scenic terrain or in the vicinity of national parks are perhaps less likely candidates for exploitation. A detailed appraisal of the economic potential and possible environmental effects of development would be needed for any of these anorthosite bodies to be considered for exploitation.

Bulk Composition and Mineralogy

Chemical analyses of anorthosites from several localities in the United States have been published (Berg 1969, Bowes et al. 1973, Crawford et al. 1971, Herz 1969, Letteney 1969, Green 1972, Nockolds 1954, Papezik 1965, Reynolds et al. 1969, Scofield 1975, and St. Clair et al. 1959). Some analyses, particularly of anorthosites in the Adirondacks, may also be found in the older literature. These analyses provide valuable



SOURCE: NRC (1977).

FIGURE 5.14 Major anorthosite deposits in the United States.

TABLE 5.9 Major Anorthosite Deposits in the United States

Name	Location		Area* (Km^2)	Minimum* Tonnage (short dry tons x 10^6)	Al$_2$O$_3$ Content* (percent)	Anorthosite (An) Content (percent)		References
	County	State				Range	Average	
San Gabriel Mountains	Los Angeles	California	215	30	27	35-55	49	Lundquist and Oakeshott (1963); Carter and Silver (1972); Ryder et al. (1975).
N.E. Delaware Piedmont		Delaware	?	?	?	35-44		Thompson (1975).
Boehls Butte	Shoshone, Clearwater	Idaho	150	2.9	29			Hietanen (1963).
Keweenawan Series	Cook, Lake	Minnesota	520	0.1	30			Phinney (1969a); Green (1972).
Duluth Complex	Lake	Minnesota				48-70	55-65	Taylor (1964); Davidson (1972); Phinney (1969a, b; 1972a, b).
Stillwater Complex	Stillwater, Sweet Grass	Montana	18	4.1	30			Bowes et al. (1973).
Bitterroot Range	Adams, Valley	Montana	>2.5	?		30-90	47-53	Berg (1969).
Adirondacks								
- Main Body	Essex, Franklin, Hamilton, Warren, Jefferson, Clinton	New York	3,300	377.0	26	50-55		Buddington (1969, 1972); Isachsen and Moxham (1969); Letteney (1968).
- Thirteenth Lake			235	11.0	26			
- Carthage			2	0.5	26			
- Rand Hill			15	2.9	25			
Wichita Mountains	Comanche, Jackson, Kiowa	Oklahoma	40	1.0	28	62-83	75	Scofield (1975).
Honey Brook	Chester	Pennsylvania	40	0.2	27		55	Crawford et al. (1971).
Roseland	Nelson, Amhurst	Virginia	<60	?		27-28	28	Herz (1969).
Mineral Lake		Wisconsin	<120	?		45-62	60	Olmstead (1969).
Laramie Range	Albany, Laramie	Wyoming	650	36.2	27	40-66		Hagner (1951); Devore (1975).

* Principal Source: U.S. Bureau of Mines (1967).

information about some accessory elements, such as titanium and potassium, that might, in some places, be recovered as byproducts. Table 5.10 summarizes the mineral composition of anorthosite.

Accessory Constituents

Few analyses of minor-element distributions in anorthosites are available. Those summarized in Table 5.10 may be far from representative, but they provide approximate concentration ranges for some elements; few accessory elements can be found at higher concentrations in anorthosites than their average abundances in the earth's crust (Turekian 1972). The only significant exception is molybdenum in Adirondack plagioclase megacrysts from Mt. Colden and Saranac Lake, New York (Isachsen and Moxham 1969), and possibly chromium at Mt. Colden and Saranac Lake and in the Stillwater Complex of Montana (Bowes et al. 1973). However, the average concentrations of these two elements in the Adirondack anorthosites are too low (near 6 and 240 parts per million, respectively) to make these deposits an economically attractive resource.

In the absence of chemical analyses, some idea of the possible accessory element content of anorthosites might be gained by study of minor elements associated with the principal mineral phases. Column 4 of Table 5.10 lists associated minor elements for the mineral species found.

Mining and Processing

Massive anorthosite bodies would be mined by large-scale open-pit methods. Because anorthosite contains no readily soluble constituents, no potentially harmful accessory elements are expected to leach from exposed rock faces or from fractured rock and contaminate surface or ground waters. Intensive leaching could lead to increased alkalinity of surface runoff due to the presence of sodium bicarbonate. This condition should be readily controllable, but further study might be required before exploitation of a particular deposit.

Open-pit mining of anorthosite could lead to blowing dust that might be environmentally hazardous, particularly in arid regions of the United States. This possibility should be investigated and preventive measures developed, if necessary.

The alkaline nature of anorthosite dictates the selection of the process to be employed in the recovery of alumina. Two suitable processes have been considered; both avoid the use of acids to separate alumina from silica. They are referred to as the lime-soda-sinter process (see Figure 5.15) and the lime-sinter-soda-leach process. The lime-soda-sinter process was tested by the U.S. Bureau of Mines through the pilot-plant stage at Laramie, Wyoming, during 1952 to 1954 and found to be feasible for full-scale production of cell-grade alumina from anorthosite (St. Clair et al. 1959).

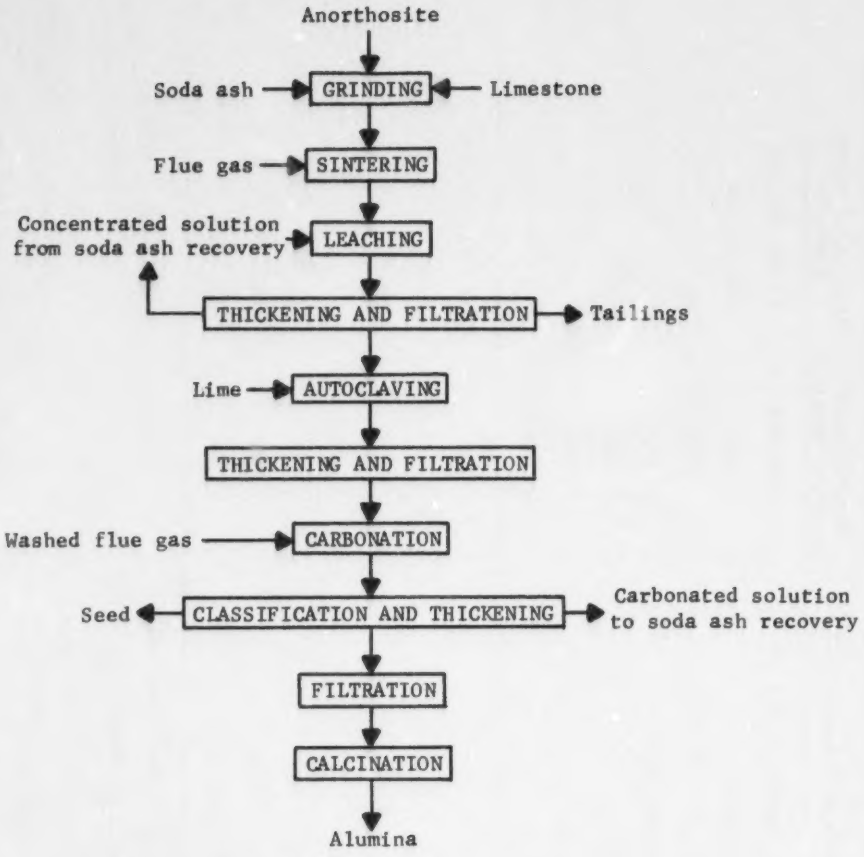
As a first step in the lime-soda-sinter process, limestone and a soda solution (NaOH and Na_2CO_3) are added to alumina-containing rock and ground to -200 mesh. The resulting slurry is dried and sintered at

TABLE 5.10 Anorthosite Mineral Composition and Accessory Elements Association

	Mineral	Stoichiometric Composition[1]	Normal Concentration Range (%)	Associated Minor Elements
PRINCIPAL MINERALS	Plagioclase	$Na[AlSi_3O_8]-Ca[Al_2Si_2O_8]$	80-100	K, Sr, Ba, Ga
	Alkali Feldspar	$(K,Na)[AlSi_3O_8]$	0-5	Na, Sr, Ba
	Clinopyroxene	$(Ca,Mg,Fe^{+2},Fe^{+3},Ti,Al)_2$	0-5	Mn
		$[(Si,Al)_2O_6]$	0-7	Ti
	Orthopyroxene	$(Mg,Fe^{+2})[SiO_3]$	0-3	
	Olivine	$(Mg,Fe)_2[SiO_4]$	0-5	
	Quartz	SiO_2	0-2	
ACCESSORY MINERALS	Magnetite	Fe_3O_4	0.1-2.5	Cr, Ni, Co, Zn
	Ilmenite	$FeTiO_3$		Ni, V
	Pyrite	FeS_2		As
	Rutile	TiO_2	tr	
	Zircon	$ZrSiO_4$	tr	U, Th
	Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	tr	RE[2], V, F, Cl
	Sphene	$CaTi[SiO_4](O,OH,F)$	tr	F
METAMORPHIC MINERALS	Hornblende	$(Ca,Na,K)_{2-3}(Mg,Fe^{+2},Fe^{+3},Al)_5$	0-3	
		$[Si_6(Si,Al)_2O_{22}](OH,F)_2$		
	Biotite	$K_2(Mg,Fe^{+2})_{6-4}(Fe^{+3},Al,Ti)_{0-2}$	0-1	
		$[Si_{6-5}Al_{2-3}O_{20}]O_{0-2}(OH,F)_{4-2}$		
	Garnet (Almandine)	$Fe_3^{+2}Al_2Si_3O_{12}$	0-2	Mg, Cr, RE[2], Mn
	Chlorite	$(Mg,Al,Fe)_{12}[(Si,Al)_8O_{20}](OH)_{16}$	0-2	
	Hematite	Fe_2O_3		

[1] Formulas from Deer et al. (1963).

[2] Rare Earths


Anorthosite
Soda ash
GRINDING
Limestone
Flue gas
SINTERING
Concentrated solution from soda ash recovery
LEACHING
THICKENING AND FILTRATION
Tailings
Lime
AUTOCLAVING
THICKENING AND FILTRATION
Washed flue gas
CARBONATION
Seed
CLASSIFICATION AND THICKENING
Carbonated solution to soda ash recovery
FILTRATION
CALCINATION
Alumina

SOURCE: Barclay and Peters (1976).

FIGURE 5.15 Block plan for processing anorthosite.

1290°C. Calcium orthosilicate and sodium aluminate are formed as the principal products of this step. The sinter is then ground and leached with more sodium carbonate solution at temperatures of 60° to 75°C, and the soluble sodium aluminate is separated from the insoluble residue. The solution is autoclaved with lime under a steam pressure of 80 pounds per square inch to precipitate excess silica, and then washed in carbon dioxide-containing flue gas at 80°C to precipitate aluminum hydroxide. Finally, the aluminum hydroxide is separated from the solution and calcined at 1230°C to produce cell-grade alumina.

The lime-sinter-soda-leach process differs from the lime-soda-sinter process in that the initial charge consists only of the rock and limestone in sufficient quantity to produce both calcium orthosilicate and calcium aluminate upon sintering. Leaching of the sinter with sodium carbonate solution leads to a reaction between the sodium carbonate solution and calcium aluminate that permits separation of soluble sodium aluminate from the calcium orthosilicate and calcium carbonate residue.

The residue from both processes consists of calcium orthosilicate, some calcium carbonate, minor quantities of alumina, sodium carbonate and sodium hydroxide not recovered during the leaching process, and miscellaneous nonsoluble minerals and their decomposition products. Because the difference between the two processes is small, discussion of the fate of accessory elements in the lime-soda-sinter process will serve for both.

Accessory constituents might affect anorthosite processing for cell-grade alumina by the lime-soda-sinter process in several ways: (1) as sources of pollution in stack or waste-water discharges; (2) as contaminants that interfere with chemical or physical treatments; (3) as impurities that degrade the quality of the final product; and (4) as important byproducts.

Although anorthosites appear initially to contain no unusual concentrations of accessory elements, some constituents may be concentrated during the lime-soda-sinter process. The stages of processing that are significant in determining the fate of accessory constituents are sintering, leaching, desilication, calcination and evaporation.

Most of the host minerals present in a typical anorthosite probably decompose during the sintering process. Volatiles such as water of hydration, hydroxyl water, carbon dioxide, sulfur dioxide from fuel combustion, and possibly some fluorine and traces of chlorine would be driven off, but subsequent scrubbing should prevent the release of large amounts of these substances to the atmosphere.

A study of phase diagrams of systems involving CaO, SiO_2 and other relevant components suggests that the probable products of sintering are akermanite ($Ca_2MgSi_2O_7$), a synthetic double oxide of calcium and ferric iron ($2CaO \cdot Fe_2O_3$), and perovskite ($CaTiO_3$), in addition to calcium orthosilicate (Ca_2SiO_4) and sodium-potassium aluminate ($[Na,K]AlO_2$). Of these phases, only $(Na,K)AlO_2$ would have significant solubility during the subsequent leaching stage. The remainder would appear in the residue. Unless additional recovery stages were added to the lime-soda-sinter process, no separation of magnesium, iron, or titanium would result.

A review of the behavior of the accessory elements found in anorthosites (Table 5.11) indicates that all would probably appear in the residue except the alkali metals and possibly gallium and scandium. The only significant negative effect accessory elements might have on the lime-soda-sinter process would be to cause slightly increased consumption of limestone feed.

The presence of silica and potassium in the cell-grade alumina product is undesirable. The relatively high solubility of silica in the alkaline leaching solution is lowered through the precipitation of calcium orthosilicate by lime during autoclaving. According to St. Clair et al. (1959) potassium can be maintained at acceptable levels in the leaching circuit through evaporation of the carbonator discharge and precipitation of sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) and glaserite ($3K_2SO_4 \cdot Na_2SO_4$). The sulfate in the glaserite originates from the burning of fuel during sintering.

The leached residue from the processing of anorthosite for alumina must be disposed of in a manner which prevents weathering. The residue would be very alkaline, and sodium carbonate would continue to leach if

TABLE 5.11 Accessory Element Distribution in Anorthosites (concentration in parts per million)

Acces-sory Element	Mt. Colden, NY (1,2)			Saranac Lake, NY (1,3)			Roseland, Va. (4)		Adirondacks, NY Marcy Facies, NY (5,6)		Adirondacks, NY Whiteface Facies (5,7)	
	Mean	S.D.*	Range	Mean	S.D.*	Range	Mean	Range	Mean	Range	Mean	Range
B	5.7	1.5	<5-10	9.3	7.1	~5-25						
Ba	324	56	155-430	274	53	187-360	1,200	1,000-1,500	302	105-490	220	120-330
Ce												
Co	3.7	2.9	<1-13.5	5.3	2.6	2-9			10	8-13	7	5-9
Cr	236	246	1.5-950	245	71	124-350			61	31-101	36	16-61
Cu	77	45	22-215	59	16	40-86	18	3-30	9	2-16	8	6-9
Ga	14	5	<4-26	24	6	13-35	15	15				
La												
Li												
Mn	—	—	150-315	161	35	98-215	150	150	389	341-453	305	229-403
Mo	4.8	3.5	<2-14	8.3	6.6	4-16						
Ni	86	61	3-188	139	37	90-205			12	7-21	6	4-9
Pb	48	84	<3-320	11	7	<5-23	22	15-30				
Rb												
Sc												
Sr	301	78	70-525	230	30	180-275	1,000	1,000	702	636-746	713	665-763
Ti	1,910	1,021	310-5,100	1,450	643	240-2,650						
V	297	116	8-630	31	15	17-57			45	40-50	42	35-48
Y	13	7	5-34									
Zn									52	20-81	37	19-65
Zr				761	116	595-920						

* Standard Deviation

SOURCE:

(1) Isachsen and Moxham (1969)
(2) Plagioclase megacrysts only (23 samples)
(3) Plagioclase megacrysts only (13 samples)
(4) Herz (1969)
(5) Papezik (1965)
(6) 3 samples
(7) 3 samples

TABLE 5.11 (Continued)

Accessory Element	Stillwater Complex, Ma. Traverse A								Stillwater Complex, Ma. Traverse B					Stillwater Complex, Ma. Traverse C			Avg. Crustal Abundance (9)
	17	18	19	20	21	22	23	24		45	46	47	48	59	60	61	
B																	9
Ba	45	120	40	95	35	45	20	25	60	60	25	70	25	100	70	50	610
Ce	40	2	0	6	20	40	20	15	65	40	50	15	10	40	45	30	74
Co	16	7	16	4	11	1	19	8	14	18	24	2	12	6	1.5	14	12
Cr	17	9	18	2	117	10	384	71	431	350	549	17	138	386	1	5	48
Cu	58	18	23	19	37	20	47	31	36	71	72	23	33	9	20	43	32
Ga	8	9	7	7	9	7	6	7	6	8	6	8	9	7	11	9	18
La	35	5	0	0	0	20	20	0	65	40	45	15	10	25	15	9	58
Li	8.0	5.5	2.1	4.5	1.4	3.6	1.4	1.6	7.2	1.9	0.7	2.2	0.7	1.5	1.1	6.6	29
Mn																	670
Mo																	1.2
Ni	52	22	86	12	71	14	140	60	116	160	216	28	70	43	16	73	37
Pb																	15
Rb	0	5	0	4	1	1	2	0	2	2	5	4	5	1	2	1	120
Sc	2	4	4	3	10	1	14	5	12	13	19	1	6	3	<1	7	14
Sr	175	175	160	185	160	175	140	160	145	180	135	180	155	130	210	180	300
Ti																	4,400
V	37	41	41	44	52	29	68	47	58	67	79	13	42	16	19	48	98
Y	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	38
Zn	5	1	9	0	7	0	9	1	7	2	6	0	1	0	1	17	63
Zr	<5	<5	0	10	<5	0	0	<5	<5	9	8	5	0	0	10	10	170

SOURCE:

(8) Bowes et al. (1973).
(9) Turekian (1972).

exposed to rainfall or other precipitation. Subaerial exposure of the residue to long dry periods would lead to problems with blowing dust. Further study to define the seriousness of these environmental problems is warranted.

Byproducts

Potassium appears to be the only accessory element involved in anorthosite processing that merits consideration. The quantity of K_2O obtainable as a byproduct from the lime-soda-sinter process depends on its concentration in the anorthosite feed. Assuming an initial concentration of five weight percent K_2O in a rock containing 25 percent Al_2O_3, and assuming recoveries of 50 and 85 percent, respectively, for K_2O and Al_2O_3, then the production of 1,000 tons of cell-grade alumina would yield approximately 120 tons of K_2O as glaserite.

The calcium orthosilicate residue from the processing of anorthosite by the lime-soda-sinter process would be particularly suitable for portland cement manufacture. Such utilization would obviate the problem of disposing of this material.

Anorthosites are in many places associated with titanium ores, either as titanomagnetite, ilmenite, or rutile. The Duluth anorthositic complex also contains copper and nickel sulfides. Apatite segregations are also found associated with anorthosites. It is possible, but unlikely, that some anorthosites might contain economically recoverable quantities of these minerals.

Conclusions and Recommendations

Accessory Element Data

Complete chemical analyses of anorthosites in the United States are not available in sufficient quantity to permit an adequate review of all potential problems or opportunities that might arise with respect to accessory elements during mining and processing. It is possible that some as yet unidentified accessory elements would have a deleterious impact during mining, processing, or disposal, or could be recoverable as beneficial byproducts.

Complete chemical analyses for all elements should be made of representative samples from all major anorthosite intrusives. Modal analyses should be made concurrently of the same material. Based on the results of these analyses, detailed studies should be made of the fate of selected accessory elements during all stages from mining to waste disposal.

Product Recovery and Waste Disposal

Open-pit mining of anorthosites is not expected to cause any environmental problems different from those associated with the mining of granite or other hard crystalline rocks. Nevertheless, attention should be paid to the leaching of waste and to blowing dust from the mining operation.

Present methods of processing anorthosites appear to be satisfactory with regard to the disposal of accessory elements. If anorthosite processing were to develop into a full-scale source of alumina, consideration should be given to improved techniques for recovery of potassium from the leach liquor, reduction of sulfate contamination, and more efficient separation of sodium carbonate from the residue. Improved leaching efficiency could lead to byproduct sodium carbonate production and higher alumina recovery.

Very little information is available about the behavior of accessory elements during sintering and subsequent leaching. Mineralogical and chemical characterization of the sinter product and leached residue should be made to ascertain the fate of those elements with uncertain histories.

Disposal of the leached residue might require precautions against continued leaching by atmospheric precipitation or wind dispersion. The leachate would be very alkaline (pH 9 to 10). The leached residue might be usable for the manufacture of portland cement.

NEPHELINE SYENITES

Nepheline syenites are coarsely crystalline igneous rocks composed of alkali feldspars and nepheline. Minor amounts of alkalic pyroxenes, other feldspathoids, and a diverse range of accessory elements constitute the remainder of the rock. Nepheline syenites belong to a family of alkaline rocks noted for higher concentrations of alkali metals and deficiencies of calcium, magnesium, and iron; those containing nepheline or other feldspathoids are also deficient in silica and enriched in aluminum.

Alkaline rocks in North America (see Barker 1974) occur as subcylindrical zoned stocks or ring complexes averaging 5 kilometers in diameter, as extensive belts of concordant bodies of gneissic nepheline syenite, or as laccoliths, small stocks, sills, or dike swarms in undisturbed or gently folded sedimentary rocks. They crop out over at least 3,000 square miles of the North American continent. However, only a small proportion (probably less than 5 percent) consist of nepheline syenites. In contrast to anorthosites, nepheline syenite occurrences are small, rarely exceeding a few square miles in area.

Resources

Nepheline syenites are broadly distributed in the Appalachian Mountains, the Ouachita Mountains, and the western United States (see Figure 5.16). Table 5.12 lists the principal nepheline syenites, the areal extent of the alkalic rocks they are associated with (or of the nepheline syenites where information was available), and their Al_2O_3 content.

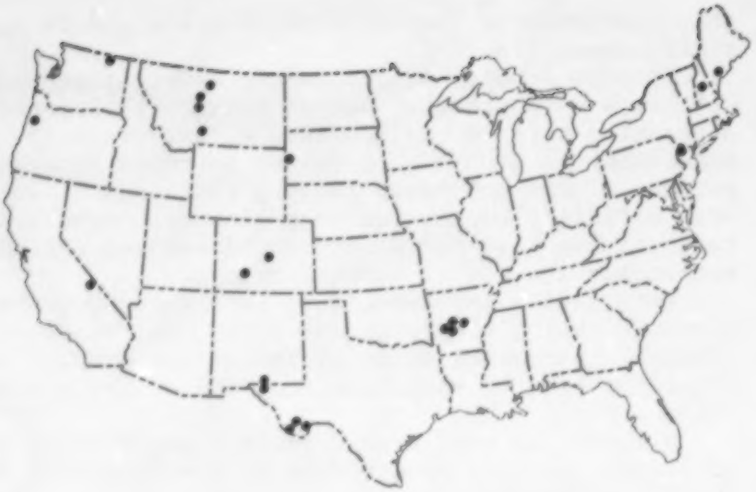


FIGURE 5.16 Major nepheline syenite deposits in the United States.

SOURCE: NRC (1977).

Bulk Composition and Mineralogy

Nepheline syenites are generally more variable in composition than anorthosites. Sodic-potassic feldspars and nepheline comprise between 80 and 90 percent of the rock. The remainder is made up primarily by alkaline pyroxene, although 5 percent or more may consist of accessory minerals, including sphene, pyrochlore, eudialite, columbotantalite, magnetite, etc.

The ratio of sodic-potassic feldspars to nepheline varies greatly, depending on the silica deficiency of the rock. Nepheline content varies from a trace to 40 percent; the greater the percentage of nepheline, the higher the aluminum content. Occasionally, nepheline is partly or wholly replaced by feldspathoids such as analcime, sodalite, melilite, nosean, hauyne, and cancrinite.

Table 5.13 gives the average compositions and concentration ranges of the minerals that make up most nepheline syenites. A representative analysis is presented in Table 5.14. Other analyses of nepheline syenites and related rock types in the United States may be found in numerous references (e.g., Csejtey and Patton 1974, Emmons 1953, Erickson and Blade 1963, Gordon et al. 1958, Jahns 1938, Jenks 1934, Larsen and Burgess 1941, Lonsdale 1940, Maxey 1976, Maxwell et al. 1967, McAllister 1952, Pecora 1942, Quinn 1937, Snavely and Wagner 1961, and Wolff 1938). Although nepheline contains 32 to 34 percent Al_2O_3, nepheline syenites have considerably less, ranging between 17 and 23 percent in domestic occurrences.

Accessory Constituents

Whether a nepheline syenite deposit is exploited for alumina might depend on its accessory constituent content. Some alkaline rock complexes contain abundant sources of rare or unusual elements; these,

TABLE 5.12 Major Nepheline Syenite Deposits in the United States

Name	Location		Area	Al_2O_3 Content	Rock Type	References
	County	State	(km^2)	(wt. percent)		
Selawik Hills		Alaska	200	22	pulaskite, juvite	Miller and Patton (1968), Miller (1972)
Granite Mountain		Alaska	9.5		nepheline syenite	Miller (1972)
St. Lawrence Island		Alaska	44*	21–23	nepheline syenite	Csejtey and Patton (1974)
Little Rock	Pulaski	Arkansas	600	18–19	nepheline syenite	Gordon et al. (1958)
Bauxite	Saline	Arkansas	12	19–21	nepheline syenite	Marks and Jackson (1975)
Magnet Cove	Hot Spring	Arkansas	12	20	sphene and garnet nepheline syenite	Erickson and Blade (1963)
Potash Sulfur Springs	Garland	Arkansas	2			Hollingsworth (1967)
Tin Mountain	Inyo	California	?	22	nepheline syenite	McAllister (1952)
Iron Hill	Gunnison	Colorado	30	?	nepheline syenite	Temple and Grogan (1965)
McClure Mountain	Fremont	Colorado	50	?	nepheline syenite	Parker and Hildebrand (1962)
South Park	Park	Colorado	?	17	analcime syenite	Jahns (1938)
Litchfield		Maine	6		nepheline syenite	Barker (1965)
Bearpaw Mountains (Rocky Boy Stock)	Hill	Montana	30*	18	nepheline syenite	Pecora (1942)
Highwood Mountains (Highwood Peak)	Great Falls	Montana	400	18	syenite	Larsen et al. (1941)

TABLE 5.12 (Continued)

Name	Location		Area	Al_2O_3 Content	Rock Type	References
	County	State	(km^2)	(wt. percent)		
Little Belt Mountains (Otter Creek)	Meagher	Montana	?		analcime-nepheline syenite	Weed and Pirsson (1899)
Crazy Mountains	Park	Montana	25	17	nepheline syenite	Wolff (1938)
Red Hill	Carroll	New Hampshire	7.4*		nepheline-sodalite syenite	Quinn (1937), Size (1973)
Beemerville	Sussex	New Jersey	2	20-22	nepheline syenite	Maxey (1976)
Cornudas Mountains (Wind Mountain)	Otero	New Mexico	8*	?	porphyritic analcime nepheline syenite	Holser (1959)
Lincoln County (Blodgett Peak)	Lincoln	Oregon	250	19	nepheline analcime syenite	Snavely and Wagner (1961)
Black Hills	Lawrence	South Dakota	25	20	phonolite	Darton and Paige (1925)
Cornudas Mountains and Diablo Plateau	Hudspeth	Texas	20	18	nepheline analcime syenite	Gross (1965), Hodges (1975), Barker (1977), Barker and Hodges (1977)
Christmas Mountains	Brewster	Texas	10	18-19	nepheline syenite	Swadley (1958), Jenkins (1959), Joesten (1977)
Terlingua-Big Bend (Sawmill Mountain)	Brewster	Texas	500	18-19	analcime syenite	Yates and Thompson (1959)
Solitario	Brewster Presidio	Texas	0.2	18	analcime syenite	Lonsdale (1940)
Shasket Creek		Washington	2	?	nepheline(?)	Parker and Calkins (1964)

*Actual areas of exposed or shallowly buried nepheline syenite. All other values relate to area of the alkalic complex as given by Barker (1969), in which the nepheline syenite may represent only a small portion of the total expanse of alkalic rocks.

SOURCE: Derived primarily from Barker (1974).

TABLE 5.13 Nepheline Syenite Mineral Composition

	Mineral	Stoichiometric Composition	Normal Concentration Ranges
Principal Minerals	Nepheline	$Na_3K[Al_4Si_4O_{16}]$	0-40
	Alkali Feldspar	$(K,Na)[AlSi_3O_8]$	90-50
	Alkali Pyroxene	$(Na,Ca)(Fe^{+3},Fe^{+2},Mg,Al)[Si_2O_6]$	5-10
	Analcime	$Na[AlSi_2O_6]\cdot H_2O$	0-10
	Sodalite	$Na_8[Al_6Si_6O_{24}]Cl_2$	0-5
Accessory Minerals	Melilite	$(Ca,Na,K)_2[(Mg,Fe^{+2},Fe^{+3},Al,Si)_2O_7]$	0-5
	Sphene	$CaTi[SiO_4](O,OH,F)$	0-5
	Apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	0-2
	Zircon	$ZrSiO_4$	0-2
	Pyrochlore	$(Na,Ca)_2(Nb,Ti)_2(O,F)_7$	0-?
	Rutile	TiO_2	0-?
	Magnetite	Fe_3O_4	0-1
	Perovskite	$(Ca,Na,Fe^{+2},Ce)(Ti,Nb)O_3$	?
	Eudialyte	$Na_4(Ca,Fe^{+2})_2ZrSi_6O_{17}(OH,Cl)_2$	?
	Columbo/tantalite	$(Fe,Mn)(Ta,Nb)_2O_6$	?

SOURCE: Ford (1949), Deer et al. (1963), and American Geological Institute (1972).

together with the potential use of a byproduct for cement manufacture, might permit the economic exploitation of these deposits as aluminum resources. In the USSR, for example, a nepheline byproduct of apatite recovery from a potash-rich syenite has been used for aluminum production, at Kirovsk on the Kola peninsula.

Semenov (1974) has reviewed the economic mineralogy of alkaline rocks. Table 5.15 summarizes the mineral deposits he has found associated with nepheline syenites and related intrusives. Other accessory elements may also prove to be significant. For example, Semenov (1974) points out that nepheline contains trace amounts of gallium, which might be extracted during alumina recovery. Lead and zinc are also widely distributed accessory elements in some alkaline rocks. Semenov cites, for example, the lujavrites of Ilimaussaq, Greenland, which contain more than .1 percent of zinc over large areas.

There are few references to accessory element distributions in nepheline syenites in the United States. Table 5.16 summarizes data from five localities and compares their accessory element concentrations with average crustal abundances as determined by Turekian (1972). The elements As, Ba, Ce, La, Mo, Nb, Pb, Sr, and V show concentrations 5 to 10 times greater than their average crustal abundances. However, only Ce, La, and Nb might have economic significance. The others can usually be found in much higher concentrations in hydrothermal ore deposits elsewhere.

TABLE 5.14 Average Composition of Nepheline Syenite

Constituent	Concentration (wt. percent)
SiO_2	53.11
Al_2O_3	21.39
Fe_2O_3	2.54
FeO	1.59
MgO	0.72
CaO	2.89
Na_2O	5.98
K_2O	9.23
H_2O^+	0.79
H_2O^-	----
TiO_2	0.83
P_2O_5	0.31
M_nO	0.12
CO_2	0.26
Cl	0.07
	99.83

SOURCE: Nockolds (1954).

Mining and Processing

Nepheline syenites and related rocks would be mined by open-pit methods. As with anorthosites, intensive leaching could lead to increased alkalinity of surface runoff, particularly since nepheline weathers more rapidly than plagioclase, and contains very little calcium. Most accessory elements would remain as insoluble residues. However, it is possible that uranium, if present, might oxidize and become mobile.

Nepheline syenites would be treated by the same lime-soda-sinter process that would be used for anorthosite. Larger quantities of limestone would be required, however, to offset the calcium deficiency of nepheline syenites. Precautions would be required to prevent blowing dust or alkaline runoff that might result from exposure of the leached residue to wind or rain.

Byproducts

Sodium and potassium might be recovered from nepheline syenite as sodium carbonate and glaserite, respectively, by fractional crystallization of the carbonated leach liquor. The quantities recovered for every 1,000 tons of cell-grade alumina would depend on the composition of the nepheline syenite and the efficiency of leaching from the sinter, but would exceed that from anorthosite because nepheline syenite contains proportionately more sodium and potassium.

If no special effort were made to recover valuable accessory elements, most would appear in the residue, including Be, Ce, Nb, P, Sr, Ti, and Zr. Lanthanum, lead, and uranium, if present in significant amounts, might leach out with the sodium aluminate and concentrate in the leach liquor. Uranium recovery from the liquor by ion-exchange methods might be profitable for some deposits. Gallium would also concentrate in the leach liquor, and might be recovered as a byproduct during recovery of excess sodium and potassium.

Recovery of many accessory elements found in nepheline syenites or related rock types would depend in large measure on modification of the lime-soda-sinter process through additional recovery stages. Many accessory elements are found in heavy minerals that could be concentrated by gravity separation from the slurry after initial grinding. Apatite, pyrochlore, perovskite, eudialyte, and zircon are examples of such minerals that would permit the recovery, respectively, of P, Ce, U, Nb, and Zr.

As with anorthosite, the residue from the recovery of alumina from nepheline syenite by the lime-soda-sinter process might be used in the manufacture of portland cement.

TABLE 5.15 Mineral Deposits in Nepheline Syenites

Rock Type	Stage	Characteristic Minerals	Characteristic Elements	Examples of Deposits
Sodalite Syenites	pneumatolic	Steenstrupine, epistolite, chkalovite, sorensenite, analcime, monazite, aegirine	Ce, Th, U, Be, Nb	Ilimaussaq, Greenland; Lovozero, USSR
Eudialite Nepheline Syenites	magmatic	Eudialyte, microcline, aegirine, rinkite	Zr, Nb, Ce	---
Urtites	magmatic	Nepheline, apatite, NbCe-perovskite, titanite, eudialyte	P, Al, Nb, Ti, Ce, Zr, F	Khibina, USSR; Lovozero, USSR
Nepheline and Alkali Syenites	pneumatolic	a. Albite, Zircon, pyrochlore, titanite, apatite, britholite	Zr, Nb, Ti, P, Ce, Ca, Na	Miask, USSR
	hydrothermal	b. Calcite, pyrochlore, apatite	Nb, P, Ca	Miask, USSR

SOURCE: Reproduced from Seminov in The Alkaline Rocks edited by H. Sorensen. Copyright (c) 1974 John Wiley & Sons Ltd.

TABLE 5.16 Accessory Element Distribution in Nepheline Syenites (concentration in parts per million)

	St. Lawrence Island, Alaska		Magnet Cove, Ark.[2]					Pulaski Co., Ark.[3]	Saline Co., Ark.			Big Iron Hill, Colo.[4]	Avg. Crustal Abundance
	1	2	MC-1[6]	L-27[6,8]	L-24[6,8]	MC-112[7]	L-54[7,8]	L-84[7,8]	1	3	5		
As			20	10	10	<10	40	10					1.7
B	70	10	0	0	0	0	0	10					9
Ba	700	500	4,000	2,000	1,000	3,300	5,000	5,000	90	2,000	30	1,600	610
Be	7	3	4	2	2	7	3	3	2	1	2		2
Ca			n.d	700	300	n.d	400	700					25,700
Ce	500	300										400	74
Co			12	20	10	8	5	10					12
Cr	2	2	130	20	10	20	5	10	--	2	--		48
Cu	<0.7	2	21	20	50	9	9	10	--	--		130	32
Fe			n.d	40,000	<100,000	n.d.	10,000	40,000					34,300
Ga	30	30	22	20	40	33	20	30	20	20	20		18
La	300	200	240	90	300	240	0	0	300	200	400	200	58
Li	700	<200											29
Mq			n.d.	3,000	2,000	n.d.	1,000	2,000					33,000
Mn			1,300	800	400	2,800	2,000	2,000	1,000	900	1,000	1,200	670
Mo	5	10	6	0	0	0	8	10	10	7	--		1.2
Nb	20	--	87	200	500	99	200	400	200	100	90	150	21
Nd	150	100											41
Ni			12	10	20	0	7	8				40	37
Pb	200	150	0	10	50	0	100	10	20	--			15
Rb												80	120
Sb			2	2	2	<1	2	2					0.3
Sc			5	10	30	3	0	0	5	5	--		14
Sn	--	--											2.1
Sr	2,000	1,500	650	1,000	1,000	540	1,000	500	200	400	200	2,800	300
Th			10	n.d.	n.d	4.5	n.d.	n.d					12

	St. Lawrence Island, Alaska		Magnet Cove, Ark.[2]						Pulaski Co., Ark.[3]		Saline Co., Ark.	Big Iron Hill, Colo.	Avg. Crustal Abundance
	1	2	MC-1[6]	L-27[6,8]	L-24[6,8]	MC-112[7]	L-54[7,8]	L-84[7,8]	1	3	5		
Ti			n.d.	10,000	40,000	n.d.	3,000	3,000	>10,000	9,000	2,000	5,000	4,400
U			2.7	n.d.	n.d.	2.7	n.d.	n.d.					2.9
V	700	30	180	200	400	520	90	500	60	50	30		98
W			10	n.d.	n.d.	<10	n.d.	n.d.					1.5
Y	100	50	36	0	30	0	20	0	200	90	100	40	38
Yb	7	3	3	0	9								3.7
Zn			100	100	100	150	500	130				60	63
Zr	500	150	400	400	400	300	200	300	700	500	300	360	170

SOURCE:

[1] Csejtey and Patton (1974).

[2] Erickson and Blade (1963).

[3] Gordon et al. (1958).

[4] Temple and Grogan (1965).

[5] Turekian (1972).

[6] Sphene nepheline syenite.

[7] Garnet nepheline syenite

[8] Analyses on saprolite.

Conclusions and Recommendations

We have little information about the mineralogy, accessory element content, and available tonnages of nepheline syenite deposits in the United States or about their suitability for alumina production. No information is available for an appraisal of the possible exploitation of nepheline syenite for recovery of both alumina and accessory elements in the same operation. On the other hand, current technology appears adequate for the recovery of alumina alone from nepheline syenites, and special recovery circuits and improved operating efficiency might also permit the recovery of valuable accessory elements. Should a nepheline syenite body be found suitable for exploitation, the potential environmental problems associated with mining, product recovery, and waste disposal would be similar to those expected in recovery of alumina from anorthosite.

The average alumina content of nepheline syenite rarely exceeds 20 percent. When compared with anorthosite, in which alumina content ranges from 25 to 30 percent, it is evident that substantial amounts of accessory elements of significant economic value would have to be present to justify exploitation. The small size of nepheline syenite deposits and their low grade make it unlikely that they will be developed for alumina in the United States in the foreseeable future.

To check these conclusions regarding the outlook for alumina extraction from nepheline syenite in the United States, the following work would be needed.

- A detailed mineralogical, chemical, accessory element, and tonnage survey of domestic nepheline syenite resources.
- Amenability tests to evaluate the suitability of the lime-soda-sinter process for use on favorable resources.
- A study of the feasibility of recovering accessory elements as well as alumina by modifications of the lime-soda-sinter process.
- An economic evaluation of nepheline syenite as an alumina resource as compared to other alumina resources.

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